REMARKS

Claims 1-8, 11 and 13-15 are pending in the present application. By this Amendment, Applicants have amended claims 1 and 14, and cancelled claim 9. Applicants respectfully submit that the present application is in condition for allowance based on the discussion which follows.

As an initial comment, Applicants respectfully submit that this Amendment After Final is appropriate for entry, as the amendment to claim 1 includes subject matter previously recited in claim 9, which previously depended from claim 1, namely that the amount of plasticizer is at least 1% and less than 10% by weight relative to the amount of titanium zeolite employed. Accordingly, the subject matter now recited in claim 1 was previously considered and examined as previous claim 9. In addition, as will be discussed in greater detail below, subject matter basis for the specific titanium zeolite powder being TS-1 was previously considered as recited in claim 2 and is further fully supported by the specification as filed. Similar amendments were made to claim 14, which recites a related method. Accordingly, Applicants respectfully submit that not more than a cursory review will be necessary in order to examine claims 1 and 14, as currently amended. Therefore, in accordance with 37 C.F.R. § 1.116, Applicants respectfully submit that this Amendment is appropriate for entry in an Amendment After Final.

Claims 1-3, 5-7, 9, 11 and 13-15 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Grosch et al. (DE 19623611) (hereinafter "Grosch"), in view of Hefele et al. (WO 98/37965) (hereinafter "Hefele"), and further in view of Sepulveda et al. (U.S. Patent No. 4,613,427) (hereinafter "Sepulveda"). In maintaining the rejection in view of the aforementioned prior art references, in the Office Action's Response to Amendment and Arguments section, it was alleged that the previously filed Declaration under 37 C.F.R. § 1.132

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(hereinafter "Strebelle Dec.") remains insufficient. As explained in the final rejection dated November 19, 2008, the Strebelle Dec. exemplifies a specific zeolite, a specific binder, a specific pore-forming agent and a specific plasticizer in specific amounts, none of which were specifically recited in combination in the claims.

Without addressing the merits of the current prior art rejections, and in order to move the case forward to allowance, by this Amendment, Applicants have amended independent claims 1 and 14 to now recite the specific titanium zeolite powder and quantity of plasticizer, in accordance with the experiments of the Strebelle Dec., and as previously recited in claims 2 and 9. As currently amended, the Strebelle Dec. fully supports the novelty and non-obviousness of the claimed invention. Subject matter basis for the amendments to claims 1 and 14 can be found in the present application as filed, including the amount of plasticizer which was previously recited in claim 9. Subject matter basis for the specific titanium zeolite powder can be found in the present specification, page 2, lines 1-4, and claim 2. Accordingly, the amendments to the claims do not constitute new matter.

Applicants respectfully submit that it will be clear from comparing the Strebelle Dec. and the present claims that the present claims are directed to a method which is fully supported by the examples of the Strebelle Dec., as further summarized below.

The additional examples submitted in the Strebelle Dec. are based on the following mixture:

- titanium zeolite powder which is TS-1,
- 4% of plasticizer (cellulose) by weight of TS-1,
- 6, 11 and 20% of binder (silicone binder) by weight of TS-1,
- 0, 10 and 20% of pore-forming substance (melamine) by weight of TS-1, and
- 60% of water by weight of TS-1.

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Amended claims now recite that in the mixture of step (a):

- the titanium zeolite is TS-1,
- the plasticizer is used in an amount from 1 to less than 10% by weight of TS-1,
- the binder is a silicon derivative binder, used in an amount of more than 5% and less than 20% by weight of TS-1,
- the pore-forming substance is used in an amount from 5 to 35% by weight of TS-1, and
- the plasticizer and the pore-forming substance are distinct from one another.

Further, although the nature of the pore-forming substance is not specifically defined in the present claims, the nature of pore-forming substances are well known in the art. Therefore, it is unnecessary to include additional details in description of these substances beyond what is described in the Strebelle Dec. Support for this can be found in the Examiner cited prior art of Hefele (e.g., column 7, lines 7-12) and Sepulveda (column 4, lines 17-21), which disclose various kinds of pore-forming substances, without identifying differences regarding their properties and, therefore, the respective inventors consider them as equivalents. Accordingly, the claimed method is consistent with the examples of the Strebelle Dec., and vice versa, to fully support the novelty of the claimed method.

In addition, the nature of the plasticizer is not specifically defined in the present claims, as, again, the prior art of Grosch (column 1, line 22-column 2, line 2) does not make a distinction between plasticizers, in accordance with its method in this art. Accordingly, in this art, further definition of the plasticizer is unnecessary in order to establish novelty, and in order to practice the invention as claimed. Therefore, the examples in the Strebelle Dec. demonstrating properties, features and advantages over the prior art are commensurate in scope with the pending claims.

Now considering that the Strebelle Dec. is commensurate in scope with the claims, Applicants respectfully submit that the Strebelle Dec. is sufficient and does demonstrate novelty and non-obviousness of the present method over the cited prior art references. Specifically responding to the Examiner's comment in the final rejection of November 19, 2008 questioning whether the example in the Strebelle Dec. with regard to the pore-forming substance produced an unexpected result as the same rate constant (k) was obtained in the absence of the use of melamine and 6 g of binder (Ex. 1) compared to 10 g of melamine and 20 g of binder (Ex. 5), Applicants respectfully submit that it appears that the Examiner has not taken into consideration that a good compromise must be found between mechanical strength (weight loss through attrition) and catalyst activity (kinetic constant related to H_2O_2). Furthermore, in view of the amended claims, Examples 1 and 5 are actually comparative examples. Indeed, in Ex. 1, <u>no pore-forming substance</u> is added and, in Ex. 5, <u>20% binder</u> is added. Thus Exmaples 1 and 5 are directed outside the scope of the amended claims in that the amended claims recite <u>more than 5% and less than 20%</u> binder.

Moreover, Applicants respectfully submit that the present claims are novel and not in any way obvious in view of the cited prior art, individually or in combination, which will be apparent based on the following discussion of the prior art references.

Grosch discloses a process for the production of epoxides using an oxidation catalyst based on titanium silicalite zeolite powder. However, Grosh is silent about the use of a pore-forming agent, especially in an amount from 5 to 35% by weight of zeolite.

Applicants respectfully note that zeolites are, by definition, porous compounds. Indeed, as explained in Appendix A, zeolites contain regular channels or interlinked voids forming pores (Appendix A, Chapter 1, § 1 "Introduction") and their principal characteristic is the well-defined

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system of regular cavities or channels (see Appendix A to these Remarks, Chapter 1, § 1, and Chapter 3.1, especially, page 3, col. 1, ¶ 2).

Furthermore, Applicants respectfully submit that Hefele does not teach or in any way describe an epoxidation catalyst or a catalyst comprising titanium zeolites, contrary to the Examiner's prior allegation. Applicants respectfully submit that the Examiner has failed to identify any portion of Hefele which discloses a titanium-based oxidation catalyst. Moreover, Hefele actually relates to coated catalysts comprising an inert-nonporous support material on which a catalytically active composition comprising titanim dioxide in an anatase modification (and vanadium pentoxide) is applied in layer form (see, e.g., Hefele, claim 1 and column 5, lines 11-16).

It must be emphasized that, contrary to the Examiner's assertion, titanium dioxide containing catalysts are completely different from titanium zeolite catalysts. Therefore, it is improper to in any way compare or equate titanium dioxide containing catalysts to titanium zeolite catalysts, especially in the field of epoxidation reactions. In fact, the titanium present in titanium zeolites of TS-1 type catalyzes epoxidation reactions, while anatase TiO_2 can only catalyze the H_2O_2 decomposition, and the existence of anatase in active TS-1 samples results in decreased hydrogen peroxide efficiencies in the epoxidation reaction (see, Appendix B, page 235, column 1 and § 1 "Introduction" and Appendix C, abstract, ¶ 3).

As will be clear to one of ordinary skill in the art, and in view of the aforementioned discussion, one of ordinary skill in the art would not combine the teaching of Grosch with the teaching of Hefele, since Hefele relates to a type of oxidation catalyst which cannot be used as an epoxidation catalyst, as claimed in the present invention. Accordingly, one of ordinary skill in

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the art would not have been led to combine Hefele with Grosch to arrive at the claimed invention.

Moreover, even if one of ordinary skill in the art would have combined the disclosure of Hefele with Grosch, one would not have been led to add pore-forming compounds to a product which is already porous, i.e. the epoxidation catalyst of Grosch. It must be emphasized that in order for two or more references to be combined in an obviousness-type rejection under 35 U.S.C. § 103(a), there must be some apparent reason why one of ordinary skill in the art would have been led to combine the cited prior art references. Stated differently, there must be some apparent reason why one of ordinary skill in the art would have modified the closest prior art reference, adding to it or removing from it various elements known in the art, to close the gap between the closest prior art and that of the claimed invention. *KSR Int'l v. Teleflex, Inc.*, 550 U.S. 398 (2007). For example, one reason would be if one of ordinary skill in the art had recognized a problem identified in the prior art and had knowledge of a benefit or solution achieved by modifying the prior art in order to arrive at the claimed invention. However, prior to the present invention, and in view of the prior art, one of ordinary skill in the art would not have known or had any reason to add pore-forming compounds to a product which is already porous. Therefore, it is not relevant that a titanium dioxide composition described in Hefele may comprise auxiliaries, such as pore-formers, or that it is known that porosity increases the available surface area of the catalyst, which would favor its efficiency, since Grosch already includes porous material. Therefore, one of ordinary skill in the art would not have seen a problem with the material of Grosch or recognized any benefit from modifying the material of Grosch, in view of Hefele. Furthermore, further increasing the porosity of the catalyst of Grosch would actually lead to a decrease in its resistance to attrition, which is not desirable or suitable.

Therefore, the art actually teaches away from increasing the porosity and, thus, away from the claimed method.

In addition, although the Examiner alleged that Sepulveda relates to catalysts prepared by extrusion, and thus alleges that it would have been obvious for one of ordinary skill in the art to combine its teaching with that of Grosch, which also relates to a catalyst prepared by extrusion, Applicants respectfully submit that, based on a complete understanding of Sepulveda, one of ordinary skill in the art would not have combined its catalyst with the method disclosed in Grosch. Sepulveda relates to the preparation of catalysts based on clay, which is a non-porous compound, and thus teaches the addition of a pore-forming substance to the composition. As for Hefele, one of ordinary skill in the art would not take the teaching of Sepulveda into account to improve the properties of the epoxidation catalyst of Grosch, as the catalyst of Grosch is, by definition, already porous and there is no motivation or teaching to lead one to further increase its porosity. Furthermore, increasing the porosity of the catalyst of Grosch would *a priori* lead to a decrease of its resistance to attrition.

In conclusion, as discussed above, and provided in the Strebelle Dec., Applicants have surprisingly found that adding a pore-forming agent in an amount of 5 to 35% titanium zeolite catalysts (which is, by definition, already porous), prepared by extrusion, improves the catalyst activity (e.g., increased kinetic constant related to H_2O_2), while the mechanical strength of the catalyst (weight loss through attrition) is not impacted or even improved, provided that a silicon derivative binder is added in an amount of more than 5 and less than 20% by weight of the titanium zeolite. Nothing in Grosch, Hefele or Sepulveda, individually or in combination, teach one of ordinary skill in the art that it is usual to or that one should increase the porosity of a zeolite catalyst which is, by definition, already porous. Furthermore, nothing in the

aforementioned cited references teach one of ordinary skill in the art that a good compromise must be found between mechanical strength and catalytic activity, where the compromise is linked to the respective amounts of binder and pore-forming substance.
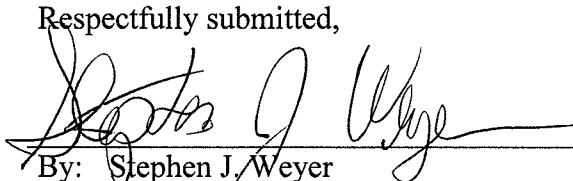
Based on the foregoing, Applicants respectfully submit that claims 1-3, 5-7, 11 and 13-15 are not obvious in view of the cited prior art.

Claims 4 and 8 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Grosch, Hefele and Sepulveda, further in view of U.S. Patent No. 5,965,476 (hereinafter "Balducci"). Applicants respectfully submit that, as discussed above with regard to the rejection of the claims in view of Grosch, Hefele and Sepulveda, the aforementioned references fail to teach or in any way make obvious the subject matter of claims 4 and 8. Further, Applicants respectfully submit that the additional cited reference of Balducci fails to teach or in any way make up the deficiencies of the aforementioned prior art references with regard to the subject matter of claims 4 and 8. Accordingly, Applicants respectfully request that the rejection to claims 4 and 8 be withdrawn.

In view of the foregoing, Applicants respectfully submit that the present application is in condition for allowance.

Respectfully submitted,

Date: May 7, 2010

By: Stephen J. Weyer
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APPENDIX A

Zeolites

ECKEHART ROLAND, Degussa AG, ZN Wolfgang, Hanau, Federal Republicof Germany

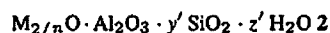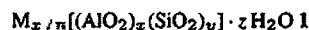PETER KLEINSCHMIT, Degussa AG, ZN Wolfgang, Hanau, Federal Republicof Germany

1. Introduction

The exact definition of the term "zeolite" is still the subject of discussion [1–4]. A version in general use is due to BARRER [1] and BRECK [5], which states that zeolites [1318-02-1] are crystalline, hydrated aluminosilicates with a framework structure. Their three-dimensional, polyanionic networks are constructed of SiO_4 and AlO_4 tetrahedra linked through oxygen atoms. Depending on the structure type, they contain regular channels or interlinked voids whose aperture diameters are in the micropore range. These pores contain water molecules and the cations necessary to balance the negative charge of the framework. The cations, which are mobile and can be exchanged, are mainly alkali metal or alkaline earth metal ions.

Formula 1 accords with these characteristics. The expression enclosed in the square brackets shows the composition of the anionic framework in the crystallographic unit cell. M represents the nonframework metal cation, and n is its charge. Formula 2 occurs frequently in the literature and, unlike Formula 1, simply represents the overall chemical composition.

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot z\,H_2O \quad \mathbf{1}$$

$$M_{2/n}O \cdot Al_2O_3 \cdot y'\,SiO_2 \cdot z'\,H_2O \quad \mathbf{2}$$

Many synthetic zeolites also occur naturally as minerals. The observation that a certain mineral began to bubble on strong heating led CRONSTEDT in 1756 to give the name "zeolites" to such materials from the Greek zeo: to boil and lithos: stone [6], [7]. However, zeolites only became of industrial importance in the 1950s, when synthetic examples became available on an industrial scale [8]. Since then, world consumption of synthetic zeolites in the fields of ion exchange, adsorption, and catalysis has grown continuously. The total for 1993 exceeded 10^6 t, mainly a consequence of the use of the zeolite NaA as a detergent builder. Zeolites are also important as adsorbents for separating and purifying substances and as catalysts in a number of important processes in the chemical and petrochemical industries.

In addition, ca. 300 000 t/a natural zeolites are sold worldwide. Their main uses are as ion ex-

changers for water treatment, in soil improvement, in animal feeds, in cat litter, and in pozzolanic cement.

The wide range of commerical applications has stimulated intensive investigation of the chemistry and physics of the zeolites [5], [9–19]. Current research is increasingly concerned with zeolite-like molecular sieves, which have expanded the field of zeolites enormously during the last two decades. In these new materials, the aluminum and silicon of the classical zeolites are partially or completely replaced by other elements [20], [21]. The most important groups of these molecular sieves are:

1) Modifications of silica ("zeosils," see → Silica, Chap. 8.2.1.)
2) Metallosilicates with tri- and tetravalent heteroatoms in place of aluminum as framework components, e.g., boro- and gallosilicates [22], ferrisilicates [23], and titanosilicates [24]
3) Alumino- and gallophosphates and compounds derived from them [25–27]

These compounds generally have framework structures analogous to those of the zeolites. Some new structures have been discovered, too. However, with a few exceptions, these compounds are still of rather limited economic importance, and are discussed here only briefly.

2. Nomenclature

The naming of zeolites in the literature seldom follows a scientific system. If natural analogs exist, the synthetic zeolites are often named after the minerals (e.g., faujasite, mordenite, ferrierite, and offretite). Alternatively, the names given by the discoverers are used. In the 1950s and early 1960s, new synthetic zeolites were named using the letters of the Latin and Greek alphabets. Examples include the Linde molecular sieves A, L, X, and Y of Union Carbide and the zeolites beta, rho, theta-1, and omega. Acronyms that indicate the industrial or university laboratory that first synthesized a given material were then increasingly used, supplemented by a consecutive numbering system. Names such as ZSM-5 (Mobil Oil), Nu-13 (ICI), LZ-210 (Union Carbide/UOP), CSZ-3 (Grace),

and ECR-1 (Exxon) have gradually become generally accepted.

Zeolites with identical framework structures can therefore appear in the literature under different names. Some order has been imposed by the introduction of a classification system in the *Atlas of Zeolite Structure Types* [28], which indicates which different materials have the same structure type. The structure types themselves are denoted by the combination of three capital letters. For example, the type LTA is found in zeolite A, FAU in the faujasites X and Y, and MFI in the ZSM-5 family of zeolites.

CAS numbers are available for only a few zeolites. Moreover, as these are rarely used, they are of little benefit in literature searches.

3. Structure, Composition, and Properties of Zeolites

3.1. Framework Structure and Positions of Nonframework Cations

The third edition of the *Atlas of Zeolite Structure Types* [28], published in 1992, describes 85 different structures, including both classical zeolites and zeolite-like molecular sieves. The majority of these structures can be represented by Formulas 1 and 2, but a few have been found to occur only as alumino- or gallophosphates.

Zeolites are classified structurally as tectosilicates [3]. The basic elements of their frameworks are TO_4 tetrahedra (T = Si, Al) linked through oxygen atoms. The description and classification of the topology of zeolites is based on the concept of larger units known as secondary building units (SBUs) [28]. These can consist, for example, of simple rings and prisms of various sizes. By combining such basic units the known zeolite frameworks can be constructed. Alternative concepts are based on more complex chains or layer structures known as structural subunits (SSUs) [29].

The most readily visualized structural units are polyhedra such as the truncated octahedra known as sodalite cages or β-cages, found in the structure of the industrially important zeolites A, X, and Y. Figure 1 shows the sodalite unit and the framework structures of the zeolites. In this representation, the tetrahedrally coordinated silicon and aluminum atoms are symbolized by
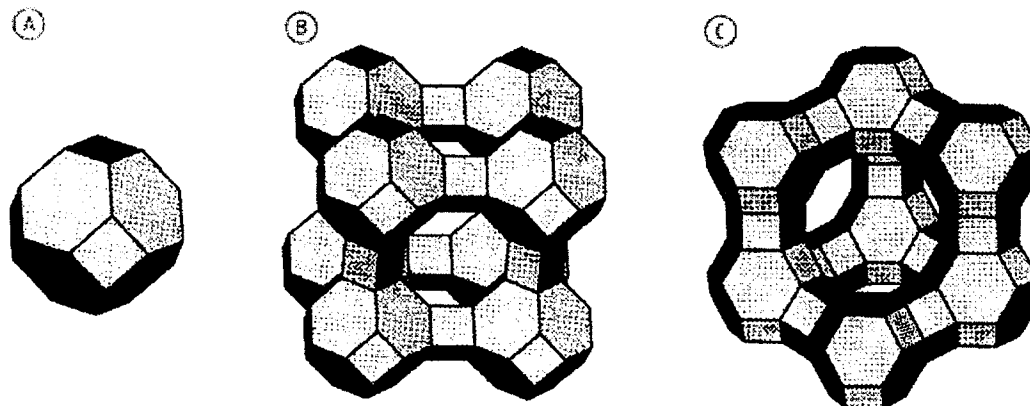
Figure 1. A) Sodalite cage or β-cage; B) Framework structure of zeolite A (structure type LTA) with α-cage; C) Framework structure of faujasite (structure type FAU; zeolites X, Y) with supercage

vertices, and the oxygen atoms are located between these.

The principal characteristic of all the structures is the well-defined system of regular cavities or channels which is essential for application of zeolites as molecular sieves. In zeolite A (type LTA), the β-cages are linked together via cubic units to form a larger cavity with the shape of a truncated cubo-octahedron. These so-called α-cages (diameter 1.14 nm) are interconnected by windows formed by rings consisting of 8 T atoms, giving a three-dimensional pore system. If the β-cages are linked together by hexagonal prisms, this results in the faujasite structure (type FAU). In this case also, the linking leads to a larger cage. This is known as a supercage because of its large diameter (ca. 1.20 nm), and has windows formed by 12 T atoms.

Whereas the cavities in the LTA and FAU structure types are characteristically in the form of interlinked cages, the MOR type (mordenite) and the MFI type (e.g., ZSM-5) contain channel systems, as shown in Figure 2. The MFI structure is easier to visualize if only the cavity structure is represented, and not the framework structure. Linear parallel ten-ring channels are linked together by zig-zag shaped continuous pores with ten-ring apertures perpendicular to the channels, resulting in a three-dimensional cavity system. In contrast, the pore system of mordenite is two-dimensional, the 12-ring channels being in effect only one-dimensional.

The various zeolite structures differ not only in the type and dimensionality of their pore systems, but also in the size of the pore apertures. Narrow-pore, medium-pore, and wide-pore zeolites have different pore apertures formed by rings of 8, 10, or 12 T atoms, with corresponding crystallographic diameters of 0.35–0.45, 0.45–0.60, and 0.60–0.80 nm [5], [30]. In the zeolites themselves, pore apertures larger than these have not so far been observed, although they do occur in the alumino- and gallophosphates, in which structures containing 14-, 18-, and 20-ring apertures are known, with diameters ranging from 0.80 to 1.45 nm [31], [32]. The pore apertures of the industrially important synthetic zeolites are listed in Table 1, together with other characteristic data for these materials [5], [30], [33]. It can also be seen from the table that the apertures can deviate to varying extents from circular. For example, the cross-section of the zig-zag pores in ZSM-5 is distinctly elliptical.

The regular nature of the pores and their apertures, whose dimensions are of the same order of magnitude as molecular diameters, enables the zeolites to function as molecular sieves. This is the outstanding property of zeolites that gives them their value as selective adsorbents for separating substances and as shape-selective catalysts (see Sections 7.2 and 7.3). Depending on the zeolite type and its pore system, molecules can penetrate into the cavity system or be excluded from it (Fig. 3).

The concepts of kinetic molecular diameter and effective pore size take account of the fact that the adsorptive molecules and the zeolite framework are not rigid, but undergo thermal vi-

brations. Therefore, the selectivity of the exclusion of molecules whose diameters are similar to that of the zeolite apertures determined crystallographically depends on temperature. Thus, the crystallographic diameter of the 6-ring aperture of the β-cage, as in type A, X, and Y zeolites, is given as 0.22 nm. However, at room temperature, water molecules with a kinetic diameter of 0.26 nm can readily penetrate into the β-cage, so that this should be regarded as the effective pore aperture.
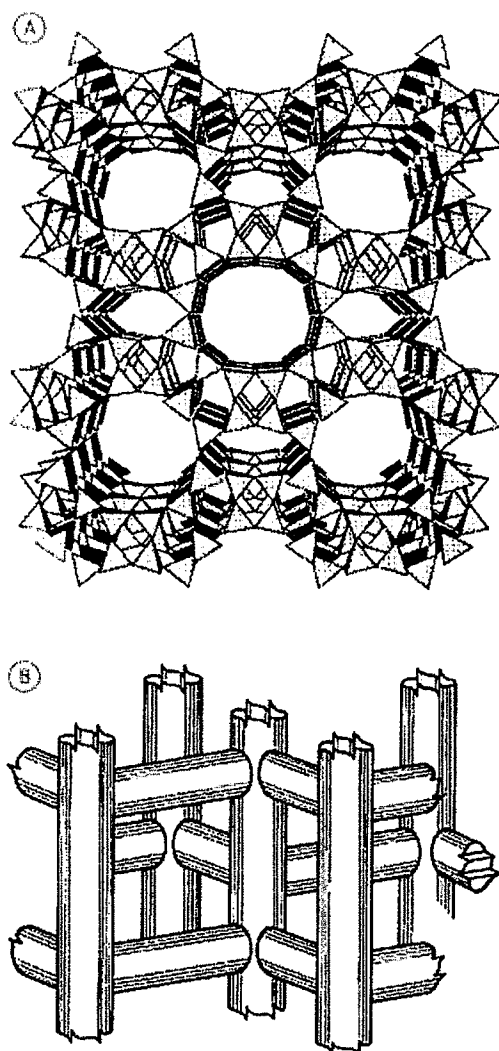

Figure 2. A) Framework structure of mordenite (structure type MOR) represented as linked SiO_4/AlO_4 tetrahedra; B) Hollow tube representation of ZSM-5 (structure type MFI)

The apparent pore diameter can also be varied by using cations of different sizes. Figure 3 illustrates this for the example of zeolites KA, NaA, and CaA.

Nonframework Cations. The cations needed to balance the negative charge on the zeolite framework occupy definite positions in the cavities and channels, where they are surrounded by partially negatively charged oxygen atoms from the rings of the framework. The framework–cation bond thus has a mainly ionic character. The preference of particular cations for particular available sites can be due to energetic, steric, and coordinative considerations [34–36]. In the presence of adsorptive molecules, a redistribution of the cations is possible. The nature and distribution of the cations in the framework are of importance when zeolites are used as adsorbents and catalysts. Any change can lead to differences in both apparent pore diameter and charge distribution.

Positions and distributions of cations in A-type and faujasite-type zeolites have been researched most thoroughly [35], [36]. In the latter type, the most important positions are the centers of the hexagonal prisms, in which octahedral coordination is possible, and positions close to the centers of the hexagonal surfaces in the supercage and β-cages (see Figure 1 C). The pattern of occupation of available sites depends on the particular cations and on whether the zeolite is anhydrous or hydrated.

A special situation arises if the zeolite is converted into the so-called hydrogen form in which the framework charge is formally balanced by H^+. In this case, acidic OH groups are bonded to the framework (see Section 7.3).

3.2. Chemical and Physical Properties

Most of the chemical and physical properties of the zeolites, and hence their areas of use, are essentially determined by the aluminum content of their frameworks. In the literature, this is usually expressed by the Si/Al or SiO_2/Al_2O_3 ratio (y/x in Formula 1 and $y' \approx 2\,y/x$ in Formula 2).

According to the Loewenstein Rule, $Al-O-Al$ groups cannot occur in crystalline aluminosilicates [37]. Hence, an SiO_2/Al_2O_3 ratio of < 2 is impossible for zeolites. As can be

Table 1. Structures and compositions of some industrially important synthetic zeolites

Zeolite	Structure type [28]	Dimenisonality of pore system	Window	Pore apertures. nm	SiO_2/Al_2O_3	Typical composition of unit cell
A	LTA	3	8-ring	0.41	2.0–6.8	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\,H_2O$
P	GIS	3	8-ring	0.31×0.45 0.28×0.48	2.0–5.0	$Na_6[(AlO_2)_6(SiO_2)_{10}] \cdot 12\,H_2O$
ZSM-5	MFI	3	10-ring 10-ring	0.53×0.56 0.51×0.55	25–∞	$(Na.TPA)_3[(AlO_2)_3(SiO_2)_{93}] \cdot 16\,H_2O$ *
X	FAU	3	12-ring	0.74	2.0–3.0	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264\,H_2O$
Y	FAU	3	12-ring	0.74	3.0–6.0	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250\,H_2O$
Mordenite	MOR	2	12-ring 8-ring	0.65×0.70 0.26×0.57	9.0–35	$Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24\,H_2O$

* TPA = Tetrapropylammonium.

Figure 3. Correlation between the effective pore size of industrially important zeolites and the kinetic molecular diameter of selected compounds (room temperature)

seen for the synthetic zeolites in Table 1, each structure type exhibits a phase breadth with respect to the SiO_2/Al_2O_3 ratio. A distinction can be made between low-silica ($SiO_2/Al_2O_3 < 4$), intermediate-silica ($4 < SiO_2/Al_2O_3 < 20$), and high-silica ($20 < SiO_2/Al_2O_3 < 200$) zeolites, and zeosils, in which aluminum is present only as a trace impurity (→ Silica, Chap. 8.2.1.) [38]. In some intermediate-silica zeolites, a higher

SiO_2/Al_2O_3 ratio can be produced by post-synthetic dealumination (see Section 6.3.2).

The aluminum atoms may not be uniformly distributed over the cross section of the zeolite crystal. More often, and especially with synthetic high-silica zeolites, a zoning effect has been observed [39], [40], which is important in catalytic applications.

Physical Properties. Synthetic zeolites containing alkali metal and alkaline earth metal cations are normally colorless crystalline powders. Colors only occur if the zeolites contain transition metals as impurities or if they have been modified by ion exchange with these elements. As a rule, the primary particles of industrially synthesized zeolites have an average size of $0.1-15\,\mu m$, although crystals with diameters of up to 5 mm can be produced under special conditions [41]. The single crystals often form larger aggregates. Like slurries of many other finely divided substances with surface-active groups, suspensions of zeolites can exhibit thixotropy or rheopexy, which is relevant in production processes.

On heating, hydrated zeolites release water. Many zeolites can be almost completely freed of adsorbed water without major alteration of their crystal structure by calcination at $400-500\,°C$, leaving solids with large free pore volumes and interior surfaces whose extent depends on the framework density of the particular structure type [28] and on the number and nature of the cations. The cavities are then available for the adsorption of guest molecules. The micropore volume of, e.g., H-ZSM-5 ($SiO_2/Al_2O_3 = 75$) is $0.18\,cm^3/g$ [42], and that of the NaA and NaX zeolites ($SiO_2/Al_2O_3 = 2.5$), including the β-cages, is as high as 0.29 or $0.36\,cm^3/g$, respectively [5].

Densities also vary with the openness of the framework structure and the nature of the cations, generally lying in the range $1.9-2.3\,g/cm^3$. If the zeolite contains heavy cations such as Ba^{2+}, densities can be higher.

The surface selectivity of the zeolites as adsorbents depends on the SiO_2/Al_2O_3 ratio. Aluminum-rich zeolites preferentially adsorb strongly polar molecules, and are therefore widely used as drying agents (see Section 7.2). Increasing silicon content leads to increasingly hydrophobic character, the transition from hydrophilic to hydrophobic behavior occurring at a SiO_2/Al_2O_3 ratio of ca. 20 [38].

Due to the mobility of the cations in their cavities and channels, zeolites exhibit ionic conductivity [5, pp. 397–410], which depends on the diameter of the channels, the nature and concentration of the cations, and the water content. Control of these parameters and a wide range of other techniques enable the conductivity properties of zeolites to be modified to make them suitable for future use as solid-state electrolytes, membranes in ion-selective electrodes, and components of cathode materials in batteries [43], [44].

Chemical Properties. In spite of their open structure, the zeolites have remarkably good thermal stability, which varies with the structure type, but more so with the SiO_2/Al_2O_3 ratio and the nature of the cations. The effect of the SiO_2/Al_2O_3 ratio is illustrated by the example of faujasite. In a low-silica NaX zeolite ($SiO_2/Al_2O_3 = 2.5$), structural collapse was observed above $660\,°C$, while a structurally equivalent NaY zeolite ($SiO_2/Al_2O_3 = 5.0$) became amorphous above $700\,°C$ [5, p.495]. Highly dealuminated Y type zeolites, however, are structurally stable at $>1000\,°C$ [45]. The effect of the cation can be seen in zeolite A, the Ca form losing its structure above $700\,°C$, and the Na form above $660\,°C$ [5, p.495]. Above the decomposition temperature, recrystallization usually occurs, e.g., forming β-cristobalite (zeolite A) or a carnegieite phase (zeolite X).

The hydrothermal stability of the zeolites, i.e., the ability to retain their structure without undergoing a phase change in the presence of water vapor, is of practical importance. For example, FCC catalysts, which contain Y-type zeolites, are used in processes where steam is used to strip off adhering hydrocarbons [46]. The same factors that affect thermal stability also influence hydrothermal stability.

Strong acids decompose low-silica zeolites such as NaA and NaX by dissolving the aluminum atoms out of the framework, with consequent breakdown of the crystal structure [47]. With increasing SiO_2/Al_2O_3 ratio the zeolites become less sensitive to dealumination by acids (see Section 6.3.2); high-silica zeolites are structurally stable even in strong mineral acids [45].

Aqueous alkalis lead to phase transitions in high-aluminum zeolites. Thus, sodium hydroxide solution converts NaA zeolite into hydroxysodalite, which must be taken into account in production (see Section 6.2). Very high silica zeolites are dissolved by strong alkalis [48].

Suspensions of high-aluminum zeolites in which the cation is Na^+ have a pH of $9-12$ due to partial hydrolysis.

(1)

The ion-exchange capacity of zeolites decreases with increasing SiO_2/Al_2O_3 ratio (see Sections 6.3.1 and 7.1). The catalytic properties of the hydrogen form, in which H^+ ions formally replace the metal ions, are discussed in Section 7.3.

4. Characterization

In principle, all methods used for investigating solids can be used for zeolites [49]. Moreover, the availability of modern physicochemical methods has significantly promoted the development of synthetic zeolites with tailored properties.

The size and shape of the zeolite crystals or aggregates must be investigated for most applications. This is carried out by microscopy, generally with a scanning electron microscope because of the small particle size. The particle size distribution can be rapidly determined by laser scattering or the Coulter counter method on zeolite suspensions.

The most important technique used to determine structure type and phase purity is X-ray diffraction (XRD). For known structures, a classification can be carried out by using the *Collection of Simulated XRD Powder Patterns for Zeolites* [50]. When structures of new materials are determined, the crystals available are seldom large enough for single-crystal X-ray structure analysis. Powder diffraction methods are therefore usual, sometimes with use of synchroton radiation [51]. The Rietveld method of profile analysis of the diffraction pattern has been developed into a very powerful tool [52]. XRD can only be used to estimate the fraction of crystalline material in a mixture with amorphous impurities in a zeolite sample by comparison with a standard material. This so-called crystallinity is

usually determined by comparing the intensities of selected reflections [53].

The thermal stability of zeolites can be determined by XRD or differential thermal analysis.

Zeolites can be analyzed for elements by classical wet chemical methods, but modern physical methods are usually preferred, i.e., X-ray fluorescence analysis (XRF), atomic absorption spectrometry (AA), and inductively coupled plasma spectrometry (ICP). X-ray photoelectron spectroscopy (XPS) is particularly useful for obtaining information about the composition of the outer atomic layers of a zeolite crystal.

The determination of the SiO_2/Al_2O_3 ratio of zeolites is of importance in many of their applications [54]. While the SiO_2/Al_2O_3 ratio of the bulk sample can easily be analyzed by the above-mentioned methods, more detailed information can be obtained by high-resolution magic angle spinning NMR spectroscopy. Thus ^{29}Si MAS-NMR spectroscopy is very suitable for determining the SiO_2/Al_2O_3 ratio of the zeolite framework, especially if the sample also contains aluminum that is not part of the framework. ^{29}Si and ^{27}Al MAS-NMR spectroscopy also gives important information on the short-range structural environment of the silicon and aluminum atoms [55–57]. Thus, the five groups $Si(OSi)_{4-n}(OAl)_n$ ($n = 0-4$) give signals with different chemical shifts in the ^{29}Si MAS-NMR spectrum. In the ^{27}Al MAS-NMR spectrum, aluminum atoms in different states of coordination give separate signals. In zeolites of the faujasite type, the SiO_2/Al_2O_3 ratio can also be estimated from measurements of the crystallographic unit cell [58] and from the position of the framework-vibration bands in the IR spectrum [59].

Information about the characteristics of the pore system can be obtained from adsorption measurements. The size of the apertures can be estimated by testing their accessibility to adsorptives of various kinetic diameters. However, determination of the inner surface area and the micropore volume from the adsorption and desorption isotherms of nitrogen is problematic [60]. ^{129}Xe MAS-NMR spectroscopy is a relatively new method of investigating the cavity systems in large-pore zeolites, the adsorbed xenon atoms acting as probes [61]. Test catalytic reactions, the outcome of which depends on the shape selectivity of the zeolite (see Section 7.3), can also be used to characterize pore systems. Depending

on the reaction, the characteristic value obtained is known as the constraint index, the modified constraint index, or the spaciousness index [62].

In the development of zeolite catalysts, it is also important to characterize their acidity properties, i.e., the nature, number, and strength of the acid sites [49], [63]. Methods include temperature-programmed desorption (TPD) of adsorbed bases such as ammonia and pyridine, ^{1}H MAS-NMR spectroscopy [64], IR spectroscopy in the region of O−H stretching frequencies [65], and measurement of the catalytic activity of the zeolites in standard reactions [63].

In addition to these general methods of investigation, zeolites are also characterized in industry by parameters that relate to a particular application. For example, where zeolites are used as detergent builders, these can include calcium binding power (determined by titration) and whiteness [66]. The suitability of a zeolite as a catalyst is determined by testing it in the reaction concerned [67].

5. Natural Zeolites

5.1. Occurrence, Mining, and Processing

Zeolite minerals occur in many rocks on the earth's surface and on the sea bed. They were first discovered in crevices and cavities in basalt flows, where they were formed by the hydrothermal decomposition of the magmatic rock. It was only in the mid-1900s that zeolites were found to occur in enormous quantities as sedimentary rock. These zeolitic tuffs were formed during various geological periods, mainly by the action of water on volcanic ash. Zeolites were also formed from poorly crystalline clays, biogenic silica, feldspars, and feldspathoids. Moreover, the less stable types of zeolite formed during the initial crystallization changed into more stable types, e.g., phillipsite or clinoptilolite in analcime.

The formation of zeolites was influenced by many specific local conditions that had to be favorable: temperature (usually in the range 25−50 °C), pressure, pH, type and concentration of salts, and availability and reactivity of silicon and aluminum sources. Suitable conditions arise in various geological or hydrological systems, which can be open or closed [17−19], [68].

Thus, zeolites occur in deposits formed from lakes with high salt or alkali contents in arid and semiarid regions. Here, dissolved sodium carbonate/sodium hydrogencarbonate can cause the pH to reach ca. 9.5. Zeolites have also been formed in alkaline soils on the earth's surface and in ocean sediments as a result of the action of percolating water, hydrothermal activity, and burial diagenesis. Depending on the system, a characteristic series of deposits varying in composition, thickness, and extent is formed. The zeolite-containing layers can be several hundred meters in depth, and can extend over areas of hundreds of square kilometers.

Of the 40 zeolitic minerals discovered in nature, clinoptilolite [12173-10-3] and the structurally related heulandite, mordenite [12173-98-7], phillipsite, chabazite [12251-32-0], erionite, analcime, and laumontite occur in the largest quantities. However, only the first six of these materials are of commercial importance at present. Information on the structures and composition ranges of these zeolites is given in Table 2.

Natural zeolites are mined in the western United States, Cuba, Japan, Slovakia, Hungary, Serbia, Bulgaria, Italy, Germany, and the CIS states, mainly by the open-cast method. Depending on the deposit, zeolites can contain other minerals as impurities, e.g., montmorillonite, cristobalite, quartz, biotite, and potassium feldspar. Mixtures of different zeolites often occur. Zeolitic minerals are processed by crushing, grinding, and classification. If they are to be used as fillers in the paper industry, wet chemical bleaching is also necessary [69].

5.2. Commercial Applications and Importance

The consumption of clinoptilolite, which has a wide range of uses, far exceeds that of any other natural zeolite [19], [70], [71]. For example, it is used in agriculture as an animal feed additive and for soil improvement (mainly in Japan). The latter application depends on two effects: it increases the pH of the soil, and, being an ion exchange material, it stores ammonium and potassium ions, thereby prolonging the activity of fertilizers. The ability to take up ammonium

Table 2. Structures and compositions of some important natural zeolites

Zeolite	Structure type [28] (dimensionality of pore system)	Window	SiO$_2$/ [Al$_2$O$_3$ + Fe$_2$O$_3$]	Most common cations	Typical composition of unit cell
Clinoptilolite	HEU (3)	8-/10-/8-ring	8.0–10.2	K > Na	(Na,K)$_6$[(AlO$_2$)$_6$(SiO$_2$)$_{30}$]·24H$_2$O
Heulandite	HEU (3)	8-/10-/8-ring	5.8–8.0	Ca, Na	Ca$_4$[(AlO$_2$)$_8$(SiO$_2$)$_{28}$]·24H$_2$O
Mordenite	MOR (2)	12-/8-ring	8.6–10.6	Na > K	Na$_8$[(AlO$_2$)$_8$(SiO$_2$)$_{40}$]·24H$_2$O
Phillipsite	PHI (3)	8-/8-/8-ring	2.6–6.8	K, Na, Ca	(Ca.K$_2$.Na$_2$)$_3$[(AlO$_2$)$_6$(SiO$_2$)$_{10}$]·12H$_2$O
Chabazite	CHA (3)	8-ring	3.4–7.6	Ca, Na, K	Ca$_6$[(AlO$_2$)$_{12}$(SiO$_2$)$_{24}$]·40H$_2$O
Erionite	ERI (3)	8-ring	6.0–7.0	K, Mg, Ca, Na	(Ca.Mg.Na$_2$.K$_2$)$_{4.5}$[(AlO$_2$)$_9$(SiO$_2$)$_{27}$]·27H$_2$O

ions is also the reason for the use of clinoptilolite and phillipsite in fish farming and cat-litter production.

If high purity, constant composition, and high capacity are not essential, natural zeolites can compete with their synthetic counterparts in a number of industrial applications. Examples include the drying of gases or liquids with clinoptilolite tuffs, and the selective adsorption of CO$_2$ and SO$_2$ by clinoptilolite or mordenite. In these applications, the stability of these zeolites towards acids is advantageous. Clinoptilolite is also sometimes used for decontaminating radioactive wastewater because of its selectivity for ^{90}Sr and ^{137}Cs ions [19], [70–72]. Natural zeolites are also used as fillers in paper and plastics, and as constituents of pozzalanic cements and lightweight building blocks.

The quantities of natural zeolites mined worldwide and the total consumption can be estimated only approximately. A figure of ca. 300 000 t/a is realistic. Japan consumes the major proportion of this, i.e., currently 130 000 t/a, while consumption in western Europe and the United States is comparatively low, namely 25 000 t/a and 15 000 t/a, respectively.

6. Production of Synthetic Zeolites

The methods used in the industrial production of solids are always influenced by the specific requirements associated with the eventual use of such materials. As this also applies to zeolites, it is normally not enough to synthesize a single-phase microcrystalline zeolite powder of definite chemical composition. Other properties are also important, such as crystallite size and morphology. Moreover, for many applications, the as-synthesized zeolite must be chemically modified by processes such as ion exchange or dealumination. Finally, for most applications in adsorption and catalysis, shaped products are required. These usually contain binders, which can impart additional properties to the product. The manufacturing of a zeolite product therefore includes much more than the actual zeolite synthesis, and consists of a well-defined series of individual steps aimed at providing a specific spectrum of tailored properties.

6.1. Zeolite Synthesis: Routes and Raw Materials

Synthetic zeolites are produced under conditions similar to those that led to formation of natural zeolites, i.e., by the mineralizing effects of water and OH$^-$ ions on reactive sources of silica and alumina in the presence of cations. However, the time required for formation of zeolites is shortened by using considerably higher temperatures and pH values. For example, high-silica zeolites are synthesized under hydrothermal conditions at temperatures exceeding 100 °C and at high pressure [73], while low-silica zeolites are usually crystallized at 70–100 °C [5], [11]. The pH is usually in the range 10–14. Reactive precursors for zeolite formation are mainly silica–alumina hydrogels produced in situ, although clay minerals are also used.

The composition of the reaction mixture is of vital significance for the synthesis process. This is usually expressed as the oxide ratio $a\,\mathrm{M}_{2/n}\mathrm{O}$: Al$_2O_3$: $b\,$SiO$_2$: $c\,$R : $d\,$H$_2$O, in

which M represents cations with charge n, and R is an organic template compound. Such compositions describe a synthesis field and lead to a specific zeolite type. Synthesis fields are often represented in a triangular diagram of the system $M_{2/n}O - Al_2O_3 - SiO_2$ (Fig. 4).
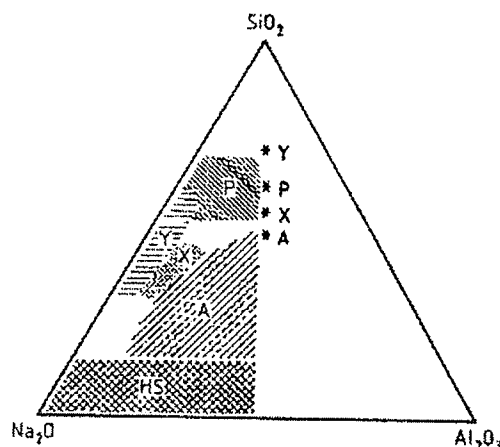

Figure 4. Synthesis fields
a Na$_2$O : b Al$_2$O$_3$: c SiO$_2$: (90 – 100) H$_2$O for various zeolites (HS = hydroxysodalite) at a crystallization temperature of 100 °C
Points marked with asterisks indicate typical compositions of the products.

6.1.1. Synthesis from Gels

In the synthesis of zeolites from hydrogels, the composition of the reaction mixture is not the only important factor. The selection of the raw materials, the way in which the reactants are mixed to precipitate the gel, and its aging influence the course and rate of the subsequent zeolite crystallization and properties of the product, such as crystal morphology.

Various silica and alumina sources can be used as raw materials. In industrial production, the cost is an important consideration apart from the fundamental suitability of the materials.

The main silica sources used for the large-scale production of zeolites are sodium silicate solutions and precipitated amorphous silicas. Silica-containing waste products from large-scale industrial processes, e.g., blast furnace slags or fly ash, have the disadvantage that they are usually contaminated with heavy metals which to some extent enter the zeolites pro-

duced. For the synthesis of expensive specialty zeolites, pyrogenic silica, colloidal silica, and esters of silicic acid such as tetraethoxysilane are used. The most common alumina source is sodium aluminate.

A further reactant is also necessary that provides OH$^-$ ions. Sodium hydroxide solution is used except for those few cases in which the presence of Na$^+$ ions prevents the formation of the desired zeolite type. Alternatively, the function of the OH$^-$ ion as a mineralizer can be performed by the fluoride ion, as has been demonstrated in a number of zeolite syntheses [74].

The synthesis of high-silica specialty zeolites often has to be carried out in the presence of organic templates. These can be alkylammonium salts, alkylammonium hydroxides, amines, alcohols, or ethers [75], [76]. The function of these additives in zeolite syntheses is not yet fully understood. A purely template effect can be excluded in syntheses in which completely different agents lead to the same structure type [76]. Often the template molecules or ions simply seem to act as space fillers. The metal cations (usually Na$^+$) in the reaction mixtures can also be assumed to exhibit a structure-directing effect.
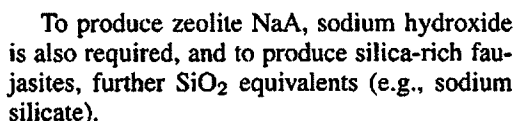
The formation of zeolites from the hydrogel that is formed by bringing together the above components is a very complex process, all details of which are not completely understood. However, the following concept is generally accepted [11], [77–80]: The gel partially dissolves during the aging process and especially when the temperature is raised to initiate zeolite crystallization. The liquid phase present with the gel becomes supersaturated, first with monomeric silicate, and then with oligomeric silicate species and aluminosilicate building blocks. The state of supersaturation ends with the formation of seeds of a metastable zeolitic phase. These then grow to form crystals.

Factors affecting the rate of zeolite formation include the reactivity of the gel, the pH, and the temperature. Increase in pH and temperature leads to increase in the rate of formation of zeolite crystals. However, the resulting zeolitic phases are metastable in their mother liquors, and the zeolite initially formed may undergo a transformation into an undesired thermodynamically more stable phase. A typical example is the formation of hydroxysodalite from NaA ze-

olite. The rate of synthesis of the zeolite can also be controlled by addition of seeds [11], [81].

6.1.2. Synthesis from Clay Minerals

Clays can also be suitable raw materials, especially for the production of the zeolites NaA, NaX, and NaY [5], [11]. The iron content of these natural materials should be as low as possible. The most important clays for zeolite production are kaolin and metakaolin, the latter being obtained by calcining kaolin at $500-700\,°C$. On further heating, spinel is formed at $>980\,°C$ and mullite at $>1050\,°C$, with formation of silica-rich phases.

$$2\,Al_2Si_2O_5(OH)_4 \quad \rightarrow \quad 2\,Al_2Si_2O_7 + 4\,H_2O \qquad (2)$$
$$\text{Kaolin} \qquad\qquad\qquad \text{Metakaolin}$$

To produce zeolite NaA, sodium hydroxide is also required, and to produce silica-rich faujasites, further SiO_2 equivalents (e.g., sodium silicate).

The synthesis of zeolites from kaolin or metakaolin is of industrial interest because its allows production of binder-free extrudates and granules (see Section 6.3.4). These shaped materials consist entirely of active substance, which is an advantage in adsorption technology. Various methods for achieving this have been described. For example [82], [83], kaolin or metakaolin is first shaped, and SiO_2 and seed crystals are added, depending on the zeolite. The zeolite is then crystallized while in the preformed shape. Alternatively, metakaolin is used as the binder as the zeolite is formed, and the binder component is then converted into zeolite by hydrothermal treatment with sodium hydroxide solution [84], [85].

In-situ production of FCC catalysts from kaolin is of major importance. The process, developed by Engelhard, has many variations [86–88]. The products are NaY zeolites in a matrix that is enriched in Al_2O_3 compared with the raw material kaolin. In one variation, microgranules containing $>40\%$ type Y zeolite are obtained [88]. For this, a slurry containing kaolin tempered at ca. $980\,°C$, water-containing kaolin, sodium silicate, and zeolite seed crystals is first spray dried, and the microgranules formed are calcined at ca. $750\,°C$, converting

the watercontaining kaolin into metakaolin. The matrix-bonded NaY zeolite is then formed by treatment with sodium hydroxide and sodium silicate at $98\,°C$. This is followed by the process that generates the active catalyst, e.g., ion exchange or ultrastabilization (see Sections 6.3.1 and 6.3.2). Thus, in contrast to other processes, the zeolite component of the catalyst is not synthesized separately.

6.2. Examples of Industrial Zeolite Syntheses

The processes and potential problems in the industrial production of zeolites [5], [89–91] are illustrated here by the syntheses of the commerically important zeolites NaA, NaY, and Na-ZSM-5.

Figure 5. Electron micrograph showing crystals of detergent NaA zeolite

Zeolite NaA [68989-22-0] is mainly used directly as a detergent builder, but is also a starting material for the production of a wide range of adsorbents (see Sections 7.1 and 7.2). An NaA zeolite detergent builder should have the following properties: high ion-exchange capacity (>160 mg CaO/g dry weight at $20\,°C$) [66] with the ability to bind ions (especially Ca^{2+}) rapidly, good dispersibility, low tendency of suspensions to settle out, low abrasive properties, and good whiteness. This means that the zeolite must consist of a single phase, as the presence of impurities such as hydroxysodalite, which forms readily along with NaA, reduces the ability of the product to bind Ca^{2+} ions. Furthermore, the average particle size must be <4 μm and the zeolite

crystals must not have sharp corners or edges. A scanning electron micrograph of a materials of this type is shown in Figure 5.

In the Degussa [92], Henkel [93], [94], and PQ processes, such a zeolite is synthesized by reacting sodium silicate containing various amounts of Na_2O and SiO_2 with sodium aluminate solutions. Clays are less often used, as the presence of impurities, especially iron, can impart an undesirable color to the product. A special variation is the Mizusawa process in which an acid-treated clay is used [95].

In the production of zeolite NaA, the stoichiometry of the reaction mixture can in principle be varied over a relatively wide range. However, efficient production requires optimization of the composition from the point of view of product quality, yield, and reaction time. A possible stoichiometry is $3.4\,Na_2O$: Al_2O_3 : $1.8\,SiO_2$: $90\,H_2O$ [93]. In this example, an excess of aluminum compared with the product stoichiometry ($SiO_2/Al_2O_3 = 2.0$) is used.

Figure 6 is a flow diagram of a process for the production of this zeolite [96]. Gel precipitation and aging are usually carried out at $50-70\,°C$. Gel precipitation is generally a batch process, but it can also be carried out continuously [94]. However, the subsequent crystallization at $80-90\,°C$ is a batch operation in stirred vessels, often $>100\,m^3$ in volume. Under these conditions, the zeolite is present in crystalline form after ca. 1 h. The suspension formed contains $120-200\,kg$ zeolite (dry basis)/m^3. The product is recovered and washed on a filter press, rotary filter, or band filter. The filter cake is slurried in water and, after the addition of stabilizers to prevent rapid sedimentation, is usually supplied to the detergent manufacturer in this form. The products are obtained in powder form by spray drying the zeolite suspension or by directly drying the zeolite filter cake.

Both the mother liquor from zeolite crystallization and the wash water are alkaline as they contain residual sodium hydroxide. If an excess of Al_2O_3 is used, sodium aluminate is also present. In this case, the filtrate is concentrated by evaporation and recycled.

The particle size, a critical parameter when the product is used as a detergent builder, is influenced by the Na_2O/H_2O ratio in the reaction mixture. High basicity favors the formation of

small particles [97]. The sequence of addition of the various components and the rate of addition during gel preparation also exert an influence. Other factors include temperature and method of stirring, especially during gel formation, and use of seed crystals [89].
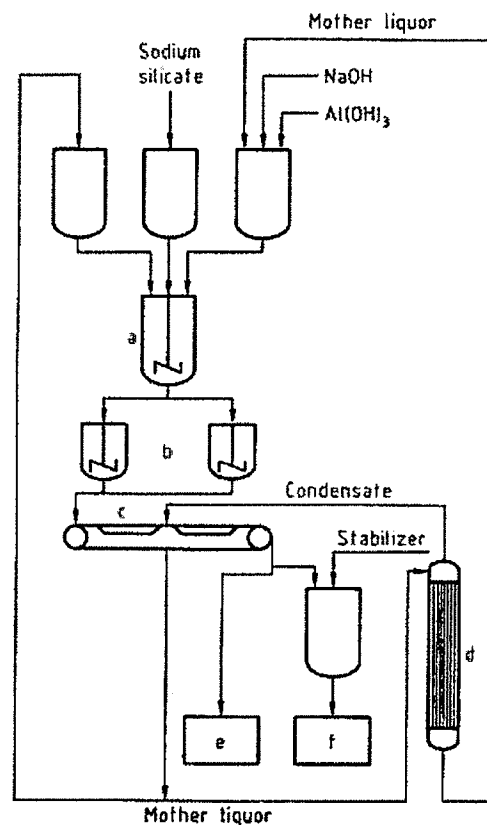

Figure 6. Process for the preparation of NaA zeolite [96]
a) Silica–alumina hydrogel precipitation; b) Zeolite crystallization; c) Filtration; d) Mother liquor evaporation; e) Zeolite spray drying; f) Stabilized suspension of NaA zeolite

Zeolite NaY is the basis for the zeolite components of FCC and hydrocracking catalysts (see Section 7.2). This raw material must have high phase purity and good crystallinity. The SiO_2/Al_2O_3 ratio should be as high as possible, as type Y zeolites modified for catalytic purposes must have good thermal and hydrothermal stability.

Commercially available NaY zeolites have an SiO_2/Al_2O_3 ratio of $5.0-5.6$. In principle, materials with higher SiO_2 content can be produced by direct synthesis, but the

necessary reduction of the Na_2O/SiO_2 and Na_2O/H_2O ratios in the reaction mixture lead to a drastic increase in crystallization time, so that such syntheses are not economic [98], [99]. Reaction mixtures with composition $(2.5-3.5)Na_2O$: Al_2O_3 : $(8.0-10.0)SiO_2$: $(120-180)H_2O$ are usually used for industrial production of NaY zeolite. The various synthetic and mineral raw materials are described in Sections 6.1.1 and 6.1.2.
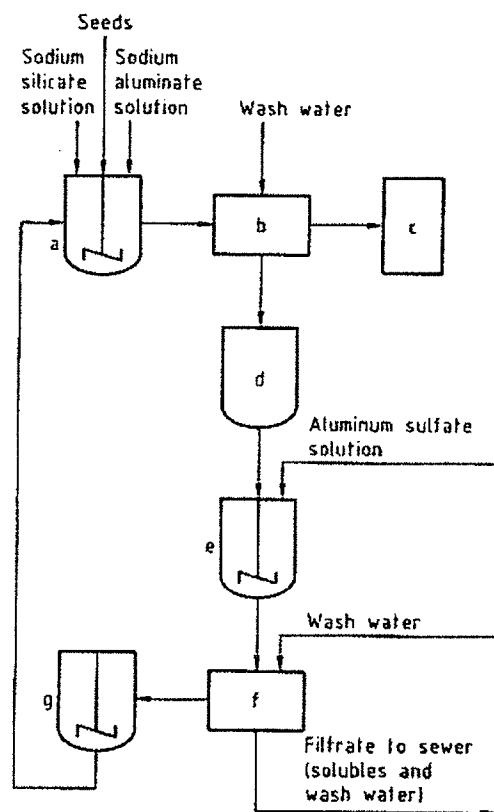

Figure 7. Process for the production of NaY zeolite [103]
a) Zeolite synthesis (gel precipitation, aging, crystallization); b) Zeolite filtration; c) Zeolite storage; d) Mother liquor and wash water storage; e) Silica–alumina hydrogel formation; f) Silica–alumina hydrogel filtration and washing; g) Silica–alumina hydrogel slurry storage

In early syntheses of NaY zeolite, the gel initially precipitated had to be aged for one or more days at room temperature. Today, seeding mixtures are generally added instead, often in colloidal form [100], [101]. They have compositions in the range $(10-16)Na_2O$: Al_2O_3 : $(10-16)SiO_2$:

$(180-320)H_2O$ and strongly influence the rate of crystallization.

The temperature during crystallization is 85 – 100 °C. Depending on this and on the composition and nature of the gel, a well-crystallized NaY zeolite can be obtained in 12–24 h. In some cases, vigorous stirring can lead to the formation of gmelinite and phillipsite as foreign phases. If the heating time is too long, this can cause transformation into more thermodynamically stable zeolites of the P or cancrinite type [102].

Figure 7 is a schematic flow diagram of a process for the production of NaY zeolite [103]. Characteristic of this process is the work-up of the mother liquor, which in the case of the synthesis of NaY zeolite is a dilute solution of sodium silicate.

ZSM-5 [79982-98-2]. As the SiO_2/Al_2O_3 ratio of ZSM-5 can vary over a wide range (see Table 1), ZSM-5, first synthesized by Mobil [104], is not a single material, but a family of zeolites of the MFI structure type [28]. The synthesis of these compounds differs from that of NaA and NaY zeolites mainly in that it is carried out at 120–180 °C in pressure vessels. ZSM-5 can be crystallized with or without template compounds [40], [73], [104–106]. Tetrapropylammonium salts are mainly used as template, but hexamethylenediamine and a series of other compounds are also suitable [75], [76]. However, the ranges of SiO_2/Al_2O_3 ratios achievable in the product by varying the initial stoichiometry by the two methods are not identical. Thus, without a structure-directing agent, SiO_2/Al_2O_3 ratios between ca. 25 and 100 can be obtained, while with template compounds a significantly wider range can be covered, i.e., from ca. 30 to the aluminum-free form (silicalite-1). Moreover, depending on the raw materials used and the exact synthesis conditions, the crystal morphology and distribution of the aluminum atoms over the crystal cross section can vary greatly [40], [73]. These parameters are of major importance in the use of ZSM-5 zeolites in catalysts.

The composition $17.1\,(TPA)_2O$: Na_2O : Al_2O_3 : $27.7\,SiO_2$: $453\,H_2O$ is a typical example of a synthesis mixture for which tetrapropylammonium bromide (TPABr) is used as the template. After 5.5 d at 125 °C, this gives ZSM-5

with a SiO_2/Al_2O_3 ratio of ca. 45 [104]. In contrast, the synthesis mixture $11.2\,Na_2O : Al_2O_3 : 70\,SiO_2 : 3213\,H_2O$, without a template and using colloidal silica as the source of silica, gives a zeolite with an SiO_2/Al_2O_3 ratio of 44 after 24 h at 190 °C [105].

The crystal suspension obtained is worked up as described above for NaA and NaY zeolite. If an organic template compound is used, it must be calcined from the ZSM-5 pores by heating to ca. 650 °C in air.

6.3. Modification and Formulation

The hydrothermal synthesis step described in Sections 6.1 and 6.2 establishes the structure type of the zeolites and the size and shape of their crystals. Only detergent zeolites are in their final form at this stage. For use as a catalyst or adsorbent, their properties must be fine tuned. This is mainly performed by ion exchange and dealumination. In addition the properties of zeolites are modified by forming them into shapes appropriate for the flow conditions under which they will be used.

6.3.1. Ion Exchange

In the production of zeolitic adsorbents, the most important techniques for increasing or decreasing the apparent pore diameter ("pore-size engineering") are those involving ion exchange [5]. An important example is the exchange of sodium ions in zeolite NaA with calcium or potassium ions. After partial replacement of ca. 30 % of the Na^+ ions by Ca^{2+}, a sudden "dilation" of the pore openings from ca. 0.38 nm (4A type [70955-01-0]) to 0.43 nm (5A type [69912-79-4], [68989-20-8]) is observed. Conversely, the replacement of ca. 25 % of the Na^+ ions by K^+ causes "narrowing" of the windows to ca. 0.30 nm (3A type [68989-21-9]).

Ion exchange is also important in the synthesis of zeolite catalysts. The aim is usually to produce Brønsted acid sites, as zeolites act as solid acids in catalysis (see Section 7.3). For certain intermediate-silica and high-silica zeolites (e.g., mordenite), the necessary ion exchange can be achieved by treatment with mineral acids. However, this method also involves the risk of

dealuminating the zeolite framework (see Section 6.3.2), and many high-aluminum species such as NaY zeolite lose their crystal structure, at least partially, at higher acid concentrations [47]. Therefore, an indirect route via an ion exchange with ammonium salt solutions must be followed. This produces the "ammonium form", which is calcined at ca. 400 °C to liberate ammonia and give the hydrogen form. In the case of zeolite Y, an acid form is also obtained by incorporating polyvalent cations, especially of rare earth metals, by ion exchange (see Section 7.3).

In the production of bifunctional zeolite catalysts that combine acidity with hydrogen-transfer capability, the inclusion of metals such as palladium and platinum is important. The first step is ion exchange with $[Pd(NH_3)_4]^{2+}$ or $[Pt(NH_3)_4]^{2+}$. The chemistry of Pd^{2+} and Pt^{2+} in zeolitic pores has been thoroughly investigated, especially in the case of zeolite Y. Calcination in the presence of oxygen to destroy the ligands followed by a heat treatment in a hydrogen atmosphere leads to formation of metal clusters of various sizes, locations, and states of dispersion, depending on the exact conditions [107], [108].

In the most widely used ion-exchange process, zeolites are treated with aqueous solutions that contain the cations to be introduced. Solid-state ion exchange in which the zeolites, usually in the ammonium or hydrogen form, are heated with crystalline salts, is as yet rarely used in industry [109], [110]. Ion exchange also occurs on impregnating zeolites with solutions of metal salts.
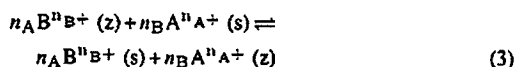
The equilibria and kinetics of ion exchange with zeolites in aqueous suspension are complex subjects in which several factors interact [5], [72], [111].

The theoretical maximum ion-exchange capacity of a zeolite is determined by its SiO_2/Al_2O_3 ratio. The true or maximum attainable ion-exchange capacity to be expected in a given case is influenced by ion-sieve and volume effects. For example, the pore apertures of zeolite X (crystallographic diameter 0.74 nm) do not permit penetration of $[N(C_2H_5)_4]^+$ ions (diameter 0.80 nm) into the cavity system. Metal cations with large, strongly bonded hydration shells such as Li^+ and Mg^{2+} cause similar problems. Nevertheless, slow ion exchange is possible in these cases, for which the cation has to

"cast off" the coordinated water molecules, at least partially. However, even in the case of wide pore apertures cations that are large in the unhydrated state still give low rates of ion exchange. The space requirements of these cations in the cavities and the need to balance the charge of the framework are then in opposition to each other.

In addition, a sieve effect within the zeolite framework can occur if the cations being exchanged are located in small and inaccessible cages. An important example of this is provided by the faujasites, in which the Na^+ ions located in the sodalite cages cannot be replaced by larger cations under mild conditions. Hence, the maximum achievable degree of exchange with rare earth cations for zeolite NaY at 25 °C is only ca. 70 % [112]. This exchange is of importance in the production of FCC catalysts (Section 7.3). It can only be carried out to completion at 180 °C under pressure. However, a different method is usually used: After achieving the degree of exchange attainable under mild conditions, the zeolite is calcined at ca. 350 °C. This causes the Na^+ ions to migrate out of the sodalite cages into the supercages where they are replaceable, and a further treatment of the zeolites with rare earth salt solutions enables exchange to be completed. The same method can be used for ammonium ion exchange [113].

In general, the ion exchange reaction for two cations A and B with charges n_A and n_B is represented by Equation (3). The symbols (z) and (s) indicate whether the cation is in the zeolite phase or in aqueous solution. The position of the equilibrium is a measure of the ion-exchange selectivity. The selectivity for given cations is determined by the electric fields of the coordinating anionic locations in the zeolite framework. Thus, for each zeolite type there is a specific selectivity series with the cations arranged in order of increasing exchangeability [5], [114].

$$n_A B^{n_B+} (z) + n_B A^{n_A+} (s) \rightleftharpoons$$
$$n_A B^{n_B+} (s) + n_B A^{n_A+} (z) \qquad (3)$$

The selectivity of an ion-exchange process involving a given cation pair is illustrated by isotherms in which the equivalent fraction of the entering cation A in solution A_s is plotted against the equivalent fraction for the same cation in the zeolitic phase A_z [5], [111], [115]. The isotherms describe the situation after equi-

librium has been reached. Figure 8 shows examples of isotherms for several cations in the ion-exchange reaction on the zeolite NaA ($B = Na^+$). For $A = Ag^+$, Ca^{2+} there is selectivity in favor of the added ions, whereas if $A = Li^+$ the equilibrium of Equation (3) always lies on the left-hand side. For $A = K^+$, the selectivity varies with the extent of ion exchange.
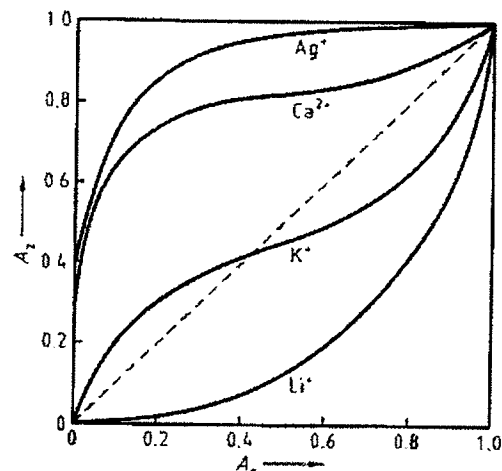
Figure 8. Ion-exchange isotherms for Li^+, K^+, Ag^+, and Ca^+ on zeolite NaA at 25 °C
Total concentration in aqueous phase: 0.1 N

Another important parameter is the pH of the exchange solution. At low pH values, H_3O^+ ions compete with the metal cations for the exchange locations. The pH must also be considered when ion exchange takes place with highly charged transition metal cations such as Fe^{3+} or Cu^{2+}, as an acidic medium is necessary here to prevent precipitation of metal hydroxides. However, slurries of low-silica zeolites such as A or X are alkaline, and these materials are unstable at low pH (see Section 3.2). These problems can often be overcome by the use of complex cations (e.g., ammine complexes).

In industry, there are many methods of carrying out an ion-exchange reaction in aqueous solution. The simplest is to suspend the zeolite in the solution under the appropriate conditions for ion exchange (amount and concentration of the salt, temperature, and pH). This is followed by filtration and washing of the filter cake. A more elegant technique is to combine these steps in a continuous process, whereby ion exchange and

washing are carried out on a band filter, for example.

A process of this kind often needs to be repeated to obtain the desired extent of ion exchange. In these cases, a process with countercurrent flow of the components is more efficient and economic [116]. The solid and the salt solution are fed in opposite directions, so that fresh unreacted zeolite comes into contact with a solution that has already been used to treat partly ion exchanged material and is therefore partially depleted in the cations to be introduced.

6.3.2. Dealumination

Dealumination increases the SiO_2/Al_2O_3 ratio of zeolites. The term is usually understood to mean the removal of aluminum from the zeolite framework, even where the overall composition of the material is unaltered or only slightly altered because the aluminum removed from the framework remains in the channels and cavities.

Dealumination is mainly carried out on zeolites with an intermediate SiO_2/Al_2O_3 ratio (see Section 3.2) that cannot be directly produced in a high-silica form and have sufficient stability to survive the sometimes drastic treatment without appreciable loss of crystallinity. The prototype for the development of dealumination methods was zeolite Y, as both its hydrothermal stability can be considerably increased and its catalytic activity for use in FCC catalysts can be modified by dealumination [45], [86], [117]. Mordenite is also often modified by dealumination [118], [119]. Dealumination is rarely used for zeolites such as ZSM-5, which can be obtained directly as a high-silica molecular sieve by hydrothermal synthesis. The catalytic properties of high-silica materials synthesized by dealumination are expected to differ from those of zeolites with the same SiO_2/Al_2O_3 ratio produced directly, as the dealumination of the structure can lead to the production of crystal defects, creation of a secondary pore system, and formation of nonframework aluminum.

A range of chemical methods [45], [117] are available for dealumination of zeolites, some of which are practiced on an industrial scale.

The simplest method is to extract aluminum with a mineral acid. This is often carried out with mordenite, which is usually produced in
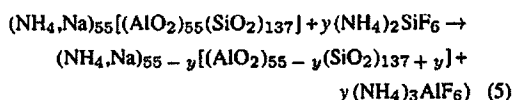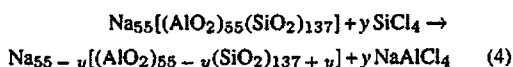
the Na form with an SiO_2/Al_2O_3 ratio of 10–12 [118], [119]. Depending on the reaction conditions, a high-silica material with a low cation content is obtained. In the case of zeolite Y, obtainable with an SiO_2/Al_2O_3 ratio of up to 6.0 by direct synthesis, this method, which causes defects, leads to considerable destruction of the framework structure. For this zeolite, the process is only suitable when used in conjunction with preliminary dealumination by another method in which not only aluminum is dissolved out of the framework but also some isomorphic replacement of aluminum by silicon takes place.

Of these methods, the steaming of Y zeolites in the NH_4^+ form (residual content of Na_2O <3–4 %) is of the greatest importance. Industrially, this is carried out at 600–800 °C in rotary kilns [46], [86], [87]. This causes aluminum atoms to migrate from the framework into the cavities, forming nonframework species. In principle, this process is a high-temperature hydrogenolysis of Si–O–Al bonds. The process causes limited damage to the structure, which can be detected by the formation of mesopores. The resulting holes are partially filled by silicon atoms from amorphous SiO_2 originating from destroyed crystal domains. The resulting zeolites have a framework structure with an increased SiO_2/Al_2O_3 ratio and very good thermal and hydrothermal stability. Today, they are of major importance as components of FCC catalysts, and are known as ultrastable Y zeolites (USY zeolites, see Section 7.3). Additional stabilization is obtained by subsequent exchange of the residual Na^+ ions with NH_4^+ ions. Nonframework aluminum species can be removed by washing with solutions of acids or alkalis [45].

In a Degussa process [120], [121], NaY zeolite is dealuminated by complete isomorphic replacement of aluminum atoms by silicon atoms using gaseous silicon tetrachloride at 250–500 °C. The reaction product $NaAlCl_4$ is removed from the cavities by washing with water. Depending on the temperature used, low-defect Y zeolites with various degrees of dealumination can be obtained. In particular this method offers a direct route to materials with SiO_2/Al_2O_3 ratios of 200 or more. These are extremely hydrophobic and are used for waste-air and exhaust gas purification (see Section 7.2). In contrast to zeolite Y, it is very difficult to

dealuminate mordenite with silicon tetrachloride [118].

Another isomorphic replacement technique is to react ammonium-exchanged Y zeolites with an aqueous solution of ammonium hexafluorosilicate [122], [123], producing thermally and hydrothermally stable Y zeolites with SiO_2/Al_2O_3 ratios of up to ca. 20. These are mainly used in FCC catalysts. Equations (4) and (5) represent the two methods, idealized for a Y zeolite with a SiO_2/Al_2O_3 ratio of 5.0.

$$Na_{55}[(AlO_2)_{55}(SiO_2)_{137}] + y\,SiCl_4 \rightarrow$$
$$Na_{55-y}[(AlO_2)_{55-y}(SiO_2)_{137+y}] + y\,NaAlCl_4 \quad (4)$$

$$(NH_4,Na)_{55}[(AlO_2)_{55}(SiO_2)_{137}] + y\,(NH_4)_2SiF_6 \rightarrow$$
$$(NH_4,Na)_{55-y}[(AlO_2)_{55-y}(SiO_2)_{137+y}] +$$
$$y\,(NH_4)_3AlF_6) \quad (5)$$

Other dealumination processes [45], [117], involving, e.g., the use of F_2, $CrCl_3$, or H_4EDTA, are not of industrial importance.

6.3.3. Other Methods of Zeolite Modification

Other less industrially important methods are known in addition to those described in Sections 6.3.1 and 6.3.2. The silanization of zeolites with mono- and disilane and the chemisorption of diborane have been thoroughly investigated. These lead to a narrowing of the pore system and to changes in the selectivity of the interior surfaces [124]. Reaction with tetraalkoxysilanes followed by calcination in the presence of oxygen only reduces the size of the pore apertures [125].

In an alternative method to ion exchange, transition metals can be introduced into the pore systems of zeolites by means of organometallic complexes [126]. In particular, socalled "ship-in-a-bottle" phthalocyanine complexes can be synthesized directly in the cavities [127].

6.3.4. Shaping

Various industrial operations for shaping other powdered materials [128–130] are also used for shaping zeolites for use as catalysts and adsorbents. These include extrusion, and granulation by the granulating pan, fluidized-bed, and spray

methods. The choice of method depends on the size and geometry most suitable for a particular application. Shaping is usually followed by drying and calcination.

To give the shaped bodies adequate mechanical stability, binders must be added to the zeolite powders. These can consist of clays such as kaolins and bentonites or synthetic materials such as amorphous silica, alumina, and silica–alumina gels. Substances that act as sources of silica, e.g., silica sols or, more rarely, esters of silicic acid, are also used in the shaping process. Binder-free shaped zeolite bodies in which the binders are transformed into zeolitic phases are a special case (see Section 6.1.2).

The selection of the type and quantity of binder must take account of the fact that the matrix in which the zeolite crystals are embedded may perform a large number of other functions in addition to its primary function, and that these may have an important effect on the property profile of the zeolitic catalysts and adsorbents. Thus, the matrix may "dilute" the activity of the zeolite, but may actually contribute to the activity of the catalyst. It can also act as a sink for sodium or vanadium ions, increasing thermal and hydrothermal stability in the case of FCC catalysts [86].

When NaA zeolite powder is granulated with water glass, the latter adheres to the pores to some extent [91], [131], leading to a reduction in the apparent pore size to ca. 0.30 nm. This effect is essential if the granulate is to be used as a drying agent in insulating glass (double glazing) (see Section 7.2).

The macroporosity of the shaped body can be influenced by the addition of certain organic compounds such as melamine. These are burnt off in a subsequent calcination stage [130].

6.4. Environmental Aspects

In the industrial-scale production of zeolites such as NaA and NaY, substances present in the mother liquors are recycled to the synthesis process (production-integrated environmental protection). The use of template compounds in the production of specially zeolites presents greater problems. The tetraalkylammonium salts and organic amines which are often used are very difficult to destroy by oxidation in the mother liquor.

There are therefore ecological as well as economic reasons to minimize the amounts of these compounds used in the synthesis.

The same is true of the metal salts used in ion-exchange processes. Here, judicious operation can be of benefit in a multistage process [116]. Dilute solutions of ammonium salts, e.g., those produced during the conversion of zeolites into the catalytically active hydrogen form, can be treated in various ways [132].

7. Applications of Synthetic Zeolites

7.1. Ion Exchange: Zeolites as Detergent Builders

The most important use of synthetic zeolites based on their ion-exchange properties is as builders in detergents. This is the largest single application of zeolites (see Chap. 8). The removal of undesired ions from wastewater is mainly carried out with the comparatively cheap natural zeolites (see Section 5.2). The treatment of wastewater from the electroplating industry with powdered NaA zeolite is an exception [133].

Pentasodium tripolyphosphate (STPP) was long regarded as the best builder for detergents on account of its excellent sequestering powers for calcium and magnesium ions and its outstanding ability to disperse soil particles. However, an intensive search for alternatives began in the early 1970s. This was driven by the discovery that a high proportion of the phosphate pollution in stationary or slow-moving natural surface waters in industrialized countries was due to the use of phosphates in detergents. In 1975, this proportion reached an average of 40 % in the Federal Republic of Germany. High phosphate levels in lakes and rivers constitute an ecological problem, leading to overfertilization, eutrophication, and excessive growth of algae, whose eventual death leads to oxygen deficiency, endangering aquatic organisms. For this reason, restrictions on the phosphate content of detergents and cleaning agents were introduced in many countries [66]. The search for a replacement lead to the development of zeolite NaA as a water-insoluble builder. It was important that the zeolite should have a small average particle size of ca. 3.5 μm and a narrow particle size

distribution, to prevent incrustations in the textile fiber. More recently, the zeolite NaP has also been used as a builder component in detergents [134], [135].

The main function of zeolite NaA used as a detergent builder is to bind ions that cause hardness [93], [96], [136–138]. The ion exchange capacity with respect to Ca^{2+} ions is ca. 160 mg CaO/g (dry basis) at 20 °C, which is comparable with that of STPP, and ca. 190 mg CaO/g (dry basis) at 90 °C, exceeding that of STPP [66]. However, the rate of reaction with Ca^{2+} ions is lower than that of the soluble builders. The corresponding relative rates are even lower in the case of Mg^{2+} ions on account of the ion-sieve effect (Fig. 9). This preference of zeolite NaA for Ca^{2+} ions is not a problem, as tap water contains considerably lower concentrations of Mg^{2+} ions than of Ca^{2+} ions.
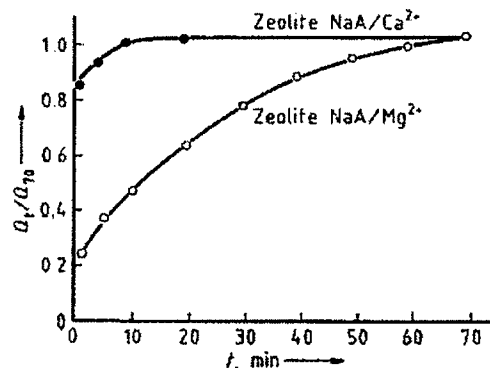

Figure 9. Ion exchange by zeolite NaA as a function of time [137]
$[Ca^{2+}]$, $[Mg^{2+}]=0 5.36\times10^{-3}$ mol/L; NaA zeolite: 1 g/L; temperature: 25 °C; Q_t: amount of Ca^{2+}/Mg^{2+} exchanged after time t; Q_{70}: amount of Ca^{2+}/Mg^{2+} exchanged after 70 min

Especially at high temperatures, the comparatively low rate of ion exchange in washing liquor, an alkaline medium, causes calcium carbonate to be precipitated before Ca^{2+} ions are taken up by the zeolite. For this reason, substoichiometric amounts of water-soluble cobuilders are added to the zeolite. In phosphate-free formulations, these generally consist of polycarboxylates in combination with sodium carbonate, and alternatively nitrilotriacetic acid, phosphonates, and citric acid. The Ca^{2+} ions in the washing liquor are initially bound to the

cobuilder, which transports them to the surface of the zeolite crystals where they are exchanged with Na^+ ions. Thus, the cobuilder acts as a carrier, and the zeolite as a means of storing Ca^{2+} ions, without which the polycarboxylates would be precipitated as calcium salts [137]. Furthermore, the cobuilder adheres to crystallization seeds of insoluble calcium salts, thereby preventing their growth (threshold effect). In Europe, phosphatefree heavy duty detergents contain 20–35 % zeolite NaA, 3–8 % polycarboxylates, and 5–20 % sodium carbonate as builder system [139]. In soft water areas such as Japan, where washing is carried out at lower temperatures (15–30 °C) than in Europe (30–95 °C), a cobuilder is not required.

The use of zeolite NaA also has positive side effects. For example, the zeolite adsorbs heavy metal ions present in trace amounts (e.g., Cu^{2+}) which impair the bleaching effect of perborate and percarbonate. Also, laundry discoloration due to adsorption of dissolved dyes, and graying due to retention of soil particles are minimized by heterocoagulation.

Extensive investigations have been carried out into the behavior of zeolite NaA in public wastewater systems and on the effects of its use on waterborne organisms and plant growth [93], [140]. No indications of harmful effects were found. A more recent study has shown that zeolite NaA in water undergoing treatment in sewage works retains the Ca^{2+} and phosphate ions present, converting them into an insoluble, relatively stable calcium aluminum silicate phosphate, and can thereby contribute to phosphate immobilization [141].

7.2. Adsorption

Along with silica gels, alumina, activated carbons, carbon molecular sieves, and organic resins zeolites are important industrial adsorbents with a wide range of uses [142–144]. Their diversity is due to the fact that zeolites not only have a high adsorption capacity but also show great selectivity, enabling substances to be separated or purified. Three effects contribute to the selectivity of a zeolite, and these can be influenced by the synthesis methods used to tailor it to requirements:

1) Zeolites are characterized by regular pores with definite aperture sizes, so that substances whose molecules are of different sizes can be separated (molecular-sieve effect, see Section 3.1). This selectivity can be influenced by post-synthetic operations, as explained in Section 6.3.1 using the example of ion exchange with zeolite NaA. The effect on the adsorption of various molecules of increasing the apparent pore size by transformation from 4A type to 5A type zeolite by calcium exchange is shown in Figure 10. Conversely, the pores can be narrowed to give 3A type zeolite by exchange with potassium salts, by steam treatment [5], or by appropriate choice of binder in the shaping process (Section 6.3.4).

2) The molecular-sieve effect described under (1) is a limiting case of kinetic selectivity, i.e., selection according to differences in the rates of diffusion of molecules into the zeolite pores.

3) The adsorption equilibrium is determined by electrostatic forces including dipole and quadrupole interactions, and also by dispersion forces. In high-alumina zeolites of types A and X (NaX is often denoted as 13X [63231-69-6] in adsorption technology) in which the negative framework charge is balanced by the appropriate number of cations, electrostatic interactions predominate. This favors adsorption by these zeolites of substances with a large dipole moment (e.g., H_2O and NH_3) or quadrupole moment (e.g., N_2). The interaction becomes stronger as the ratio of charge to radius of the cation concerned increases. In contrast, adsorption on high-silica zeolites is due only to van der Waals forces. The bonding affinity of adsorptive molecules is approximately proportional to their polarizability and therefore to their molecular mass. This is the reason for the hydrophobic surface of zeolites of this type (see Section 3.2). The interactions are especially favorable in this case if there is close contact between the pore walls and the adsorbed molecule.

Zeolites are used in adsorption technology both in gas and liquid phases. Processes can be classified according to the method of regenerating the loaded adsorbent and the method of

making the contact between the fluid and the adsorbent [142], [143]. In practice, pressure swing [145], [146] and temperature swing adsorption (PSA and TSA methods) are preferred. More rarely, desorption is carried out with a purge gas or displacement auxiliary at constant temperature and pressure (purge swing).
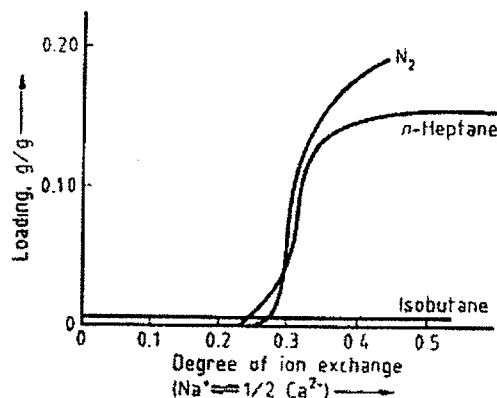

Figure 10. Effect of calcium ion exchange on zeolite NaA [5]
N_2 adsorption: 2.0 kPa, −196 °C; n-heptane adsorption: 6.0 kPa, 25 °C; isobutane adsorption: 53.3 kPa, 25 °C

Processes can also be divided into purification processes in which an undesired low-concentration component of a mixture of substances is adsorbed, and separation processes in which the components of the mixture are present in comparable amounts. The adsorption of water from gases and liquids is in fact a purification process, but, in view of its great economic importance, is discussed separately.

Static and Dynamic Adsorption of Water. Dehydrated ("activated") zeolites of types A and X are widely used in industry as drying agents in closed or open systems, i.e., for the static or dynamic adsorption of water. Their use is favored if small amounts of water have to be removed from gases or liquids. The adsorption isotherms in Figure 11 show that, unlike silica gel, zeolite NaA is able, for example, to reduce the dew point temperature of the gas to extremely low values. However, as water is very strongly adsorbed and is therefore difficult to desorb, zeolites cannot be considered for coarse drying in regenerative processes.

In drying operations, measures must often be taken to prevent larger molecules from be-

ing adsorbed and possibly undergoing catalytic reactions. This can be achieved using 3A zeolite whose pore diameter has been reduced to ca. 0.30 nm, e.g., in the drying of alkenes.
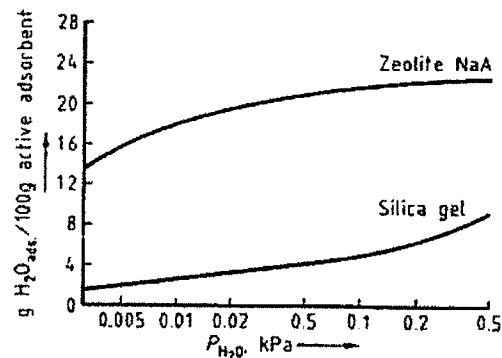

Figure 11. Adsorption isotherms for H_2O at 25 °C on zeolite NaA and silica gel at low partial pressures

A similar situation exists for the removal of atmospheric moisture from the panes of insulating glass [147], an important example of static adsorption. Here, the coadsorption of nitrogen and oxygen or insulating gases such as argon and SF_6 is undesired. Other examples of static adsorption of water by type A zeolites are the drying of coolant cycles and removal of moisture from solvent-free, noncellular polyurethane systems, in which reaction of the isocyanate component with water, forming CO_2 bubbles, must be avoided [148]. In this case, the zeolite powders remain in the cast resins, or sealing and coating compounds.

Dynamic water-adsorption processes include drying of air, natural gas, cracked gas, alkenes, and organic solvents using TSA and PSA methods with type A zeolites as the sorbents [5], [143], [145], [149], [150].

The large amount of heat liberated during the adsorption of water by high-aluminum zeolites could in future be used for zeolite-based heat storage and heat pumps. If, in another arrangement, a water reservoir were brought into contact with an activated low-silica zeolite via the gas phase, the evaporation, accelerated by the presence of the zeolite, would cause a large drop in temperature. This effect could be used for cooling [151].

Purification of Air and Gases. Zeolites of types A and X are well established in purifica-

Table 3. Commercial purification processes with synthetic zeolitic adsorbents (excluding drying)

Components removed	Crude gas	Zeolites	Refs
CO_2	natural gas. air	4A. 5A. X	[144]
H_2S, organic sulfur compounds	natural gas. hydrogen	5A	[142]
SO_x, NO_x	waste air from H_2SO_4/HNO_3 plants	not published	[154]
Solvents. odoriferous substances	industrial waste air	dealuminated Y zeolites, silicalite-1	[152], [155]
Dioxins	waste air from incinerations	dealuminated Y zeolites	[156]
Hg	natural gas, cracked gas. hydrogen, naphtha	modified Y zeolites	[157]
	waste gas from incinerators		[153]

tion processes (Table 3). They are used to remove carbon dioxide from gas streams [144], and also to remove H_2S and organic sulfur compounds, mainly from natural gas. Problems can arise in H_2S adsorption if CO_2 is also present, as this reacts with H_2S on the zeolite to form COS [142]. As the activity of calcium-exchanged zeolite A is less than that of zeolite NaA in this reaction, 5A sieves are mainly used in this process.

The removal of solvents, dioxins, and elemental mercury from moist waste-air and exhaust-gas streams by hydrophobic, high-silica zeolites such as dealuminated Y zeolite is a relatively new field [152], [153]. Compared with other adsorbents, these materials have the advantage of high thermal capacity, nonflammability, low catalytic activity, and pronounced hydrophobic properties. Regeneration is possible even if the compounds adsorbed have high boiling points or can form polymers as the zeolite absorbent can be treated at high temperatures. Moreover, they are structurally stable in the presence of acidic components, such as SO_2 and HCl in incineration off-gases.

Separation of Substances. Zeolitic adsorbents of the 5A type are used in a number of important industrial processes for the separation of mixtures of substances (Table 4). They are alternatives to carbon molecular sieves and activated carbons for the recovery of hydrogen from reformer, refinery, and coke-oven gases in various PSA processes [146], [150], [158], [159]. Here, the separation effect is based on the fact that the gaseous components listed in Table 4 are adsorbed better than hydrogen.

The production of oxygen from air by vacuum pressure swing adsorption (VPSA) processes (→ Oxygen, Chap. 4.2.) represents a growing market for zeolites. Type 5A molecu-

lar sieves are mainly used, but the use of specially optimized lithium-containing X zeolites is increasing [146], [150], [160–162]. The separation of O_2 from N_2 is possible with these materials because the nitrogen molecule, which has a quadrupole moment, is more strongly bound than the oxygen molecule. The purity of the oxygen produced can exceed 95 %, but argon cannot be separated. VPSA processes are more economic than the cryogenic production of oxygen for flexible small to medium-sized plants [161].

The O_2/N_2 separation on 4A zeolite to produce nitrogen is based on the kinetically preferred adsorption of the smaller O_2 molecules. This process is hardly used on an industrial scale, but zeolites can be useful for oxygen removal in the production of ozone [146].

The separation of n-alkanes from iso-alkanes on 5A zeolites is of importance in the mineral oil industry. For example, PSA processes have been developed by UOP (Isosiv), Texaco (TSF), Leuna (Parex-Leuna), ELF (N-Iself), Exxon, and BP [142], [146]. In these processes, regeneration is sometimes performed by displacement media such as NH_3 or short chain n-alkanes. The Molex process of UOP is a liquid-phase process designed on the principle of simulated countercurrent chromatography (Sorbex technology) [163], [164]. All these processes are based on the fact that n-alkanes are adsorbed by 5A zeolites, while iso-alkanes are too bulky to enter the pore system (see Fig. 10) and therefore break through immediately.

Sorbex technology is also used for separating xylene isomers (→ Xylenes, Chap. 4.2.2.), alkenes from alkanes, and fructose from glucose (Parex, Olex, and Sarex processes of UOP) [163]. These separations, which take place on modified zeolites of the faujasite type, are due to the selectivity of cation – adsorpt interactions.

Table 4. Some important commercial separation processes with zeolitic adsorbents

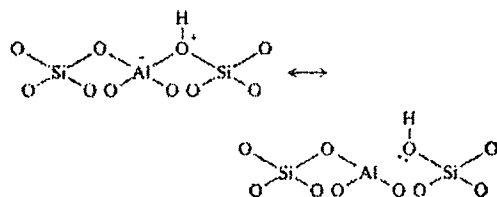| Process	Mixture	Phase *	Technology	Zeolites	Refs.
H_2 production by removal of other gases (e.g., N_2, CH_4, CO, SO_2, H_2O, O_2, CH_4, C_2H_6)	reformer, refinery, and coke-oven gases	G	PSA	5A	[146], [150], [158], [159]
O_2 production	air	G	VPSA **	5A, modified X zeolites	[150], [160–162]
Ozone production	O_3/O_2	G	PSA	not published	[146]
Separation of n- from iso-alkanes	C_6-C_{10} distillate	G	VPSA **	5A	[142]
	$C_{10}-C_{18}$ kerosene	G	purge swing	5A	
	C_5-C_6, $C_{10}-C_{15}$, $C_{10}-C_{23}$ hydrocarbons	L	Sorbex (Molex)	5A	[163]
Separation of xylene isomers	C_8 aromatics	L	Sorbex (Parex)	Sr/BaX	[163]
Separation of alkenes from alkanes	C_8-C_{18} hydrocarbons	L	Sorbex (Olex)	Ca/SrX	[163]
Fructose/glucose	molasses, hydrolyzed starch	L	Sorbex (Sarex)	CaY	[163]

* G = gas phase. L = liquid phase.
** Vacuum pressure-swing adsorption.

As well as the industrial-scale processes mentioned, there is a growing list of potential separation processes based on zeolitic adsorbents, some of which are at the pilot plant stage.
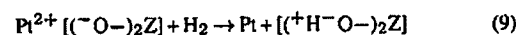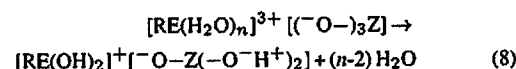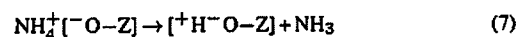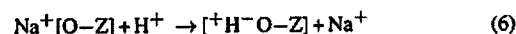
7.3. Catalysis

Apart from the very alumina rich types such as A and X, which are unstable in acidic media, zeolites can be transformed into the hydrogen form [47]. In this form, they are solid acids which can show both Brønsted and Lewis acidity [165–168]. Brønsted acid sites are protons attached to framework oxygen atoms.

The number and strength of these sites depends on the SiO_2/Al_2O_3 ratio in the framework. Decreasing framework aluminum content is associated with a decrease in the number of acidic OH groups, but generally the strength of the remaining sites initially increases [168], [169]. Structurally related zeolite-like materials in which aluminum is isomorphously replaced by gallium or boron have weaker Brønsted acidity.

Methods used industrially to produce Brønsted centers include:

1) Careful ion exchange of intermediate-silica and high-silica zeolites (e.g., mordenite) with mineral acids (Eq. 6)
2) Removal of ammonia from the ammonium form at ca. 400 °C (Eq. 7) or the decomposition of tetraalkylammonium cations
3) Ion exchange with polyvalent cations, usually of rare earth (RE) metals, followed by a dehydration (Eq. 8)
4) Reduction of noble metal cations with hydrogen (Eq. 9)

$$Na^+[O-Z] + H^+ \rightarrow [^+H^-O-Z] + Na^+ \qquad (6)$$

$$NH_4^+[^-O-Z] \rightarrow [^+H^-O-Z] + NH_3 \qquad (7)$$

$$[RE(H_2O)_n]^{3+} [(^-O-)_3Z] \rightarrow$$
$$[RE(OH)_2]^+[^-O-Z(-O^-H^+)_2] + (n-2)H_2O \qquad (8)$$

$$Pt^{2+}[(^-O-)_2Z] + H_2 \rightarrow Pt + [(^+H^-O-)_2Z] \qquad (9)$$

$[(^-O-)_nZ] =$ zeolite framework

Calcination of the hydrogen form above ca. 400 °C causes decomposition of the acidic hydroxyl groups with liberation of water. This dehydroxylation leads to formation of Lewis acid sites. As dehydroxylation takes place at similar temperatures to those used in deammoniation (Eq. 7), both types of acidic sites may be formed at the same time. The question

whether these consist of three-coordinate Al or Si sites within the framework structure or of AlO$^+$ species outside the framework structure continues to be the subject of debate [168].

Base catalysis by modified zeolites has not yet been used in industry. Suitable zeolites are ion exchanged with rubidium and cesium ions or contain sodium clusters or cesium oxide as active species in their pores [170]. Bifunctional catalysts in which the acidity of the zeolites is combined with the hydrogen-transferring function of noble metals are important in large-scale industrial processes such as hydrocracking or C_5/C_6 alkane hydroisomerization (see below).

A unique feature of the use of zeolites as catalysts is that the reactions can be shape-selective [166], [171], [172]. Shape selectivity in catalysis is closely related to the molecular-sieve effect in adsorption. Thus, it can occur if the pores of the catalyst have similar dimensions to those of the molecules or transition states taking part in the reaction:

1) In reactant shape selectivity, only reactants that can penetrate into the pore system by virtue of their slender shape and which can thus diffuse to the catalytic sites of the interior surfaces take part in the reaction

2) If the more bulky of two possible products is not formed, this is known as product shape selectivity

3) Restricted transition state shape selectivity occurs if the reaction pathway in the zeolite is directed by spatial requirements of the possible transition states

In (1) and (2), the selectivity is ultimately a result of diffusion limitation.

Shape selectivity has so far mainly been observed in reactions in which the catalyst is ZSM-5. However, the phenomenon is not limited to the use of this material, as shown by shape-selective reactions on erionite, ferrierite, mordenite, and other zeolites and zeolite-like materials.

Zeolite catalysts are used in four fields of technology:

Oil Refining. Zeolite-containing catalysts play a central role in several oil-refining processes (Table 5) [173], [174]. The most important is fluid catalytic cracking (FCC), which converts vacuum distillates and residues into gaseous alkenes, gasolines, and diesel fuel.

Y type zeolites have been used as active components in FCC catalysts since 1964 [46], [86], [175]. These materials constitute 5 – 40 % of the catalyst, which is spray granulated to give a mean particle size of 60 μm.

Table 5. Zeolite catalysts in oil refining

Oil fraction	Zeolite-catalyzed process	Zeolites
Naphtha	C_5/C_6 alkane isomerization	Pt/H-mordenite, H-ZSM-5
	reforming of C_6/C_7 alkanes	Pt/K-L, Pt/BaK-L
	M-forming	H-ZSM-5
Gas oil, lubricating oil	dewaxing/hydrodewaxing	H-ZSM-5, Pt/H-mordenite
	hydrogenation of aromatics/hydrodecyclization	noble metal – zeolite
Vacuum distillates, residues	FCC	RE-HY, USY, H-ZSM-5
	hydrocracking	Pd-, Pt-, Ni/Mo-, Ni/W-USY
	residue hydroprocessing	specially modified USY zeolites

The zeolite catalysts have higher activity and give higher gasoline yields and less coke formation than the amorphous alumina – silica and high-alumina catalysts formerly used. Today, mainly USY zeolites (see Section 6.3.2) are chosen for FCC catalysts. The extensive use of USY zeolites has reduced the consumption of RE-HY zeolites [83984-84-3] in this application. Hybrids of the two types are also used. The trend towards the use of USY zeolites, which began in the early 1980s, was a result of the prohibition of tetraalkyllead compounds as antiknock agents, necessitating an increase in the octane number of gasoline. The disadvantage of RE-HY zeolites is their high activity with respect to hydrogen transfer between alkenes and naphthenes, which leads to the formation of aromatics and alkanes. The latter lower the research octane number (RON) and motor octane number (MON) of the gasoline. The use of the less active USY types avoids this effect, which has been explained in terms of the greater distance between the active sites. Moreover, the USY types have higher hydrothermal stability and give a further reduction in coke formation and an increased gasoline yield.

There has been much discussion of the use of ZSM-5 as an additional catalyst, mainly in combination with RE-HY catalysts. ZSM-5 is

generally used in the form of a separate spray-granulated material with a binder content of ca. 75 %. The proportion of this zeolite in the total catalyst formulation is 0.5–3.0 %. The original aim was "octane boosting" by shape-selective cracking of unbranched hydrocarbons. Addition of ZSM-5 led to an increase in RON but does not always affect MON. However, another interesting effect is the increase in the proportion of C_3/C_4 alkenes, mainly propene, in the product spectrum. These alkenes can be used, for example, in the alkylation of isobutane, and can thus contribute to the increase in the octane number of the gasoline pool. However, the use of ZSM-5 does cause a slight reduction in the gasoline yield on cracking. Besides ZSM-5, other zeolites, such as beta, have been tested for possible use in the FCC process [46].

Residues from the distillation of crude oil contain high molecular mass carbon compounds and are contaminated with nickel, vanadium, sulfur, and nitrogen compounds. When these residues are cracked – a process that will increase in importance – basically the same zeolites are used as those for the catalytic cracking of gas oils [86], [176]. The main differences are in the catalyst matrix, which must have large pores and be catalytically active to precrack large molecules. The matrix must also contain additives to bond with the metals and chemically reduce SO_x, and promoters of CO oxidation.

In the hydrocracking process, an alternative to catalytic cracking, low-grade, high-boiling gas oils are converted into fuels, mainly kerosene and diesel. In this process, which is flexible with respect to the product spectrum, the majority of the catalysts used today are bifunctional, consisting of USY zeolites doped with palladium, platinum (ca. 0.5 %), or combinations of base metals such as nickel – molybdenum and nickel – tungsten [177]. The zeolite content of the catalysts is 5 – 80 %. To protect the hydrogenation components, conventional HDS/HDN (hydrodesulfurization/hydrodenitrogenation) catalysts for the removal of organic sulfur and nitrogen compounds are used prior to the hydrocracking catalysts. Specially modified Y zeolites, e.g., Fe-USY impregnated with Co/Mo, seem to be particularly suitable for the hydrocracking of residues [178].

To supply the current demand for fuels low in aromatics, new processes in which straight-run middle distillates are subjected to hydrogenation have been considered. Noble metal – zeolite catalysts that are stable towards sulfur and nitrogen compounds are used to hydrogenate or hydrodecyclize the aromatics [179].

Catalytic dewaxing is a technology for shape-selective cracking of n-alkanes in gas and lubricating oils to reduce the pour point of waxlike raw materials to temperatures below the usual limit of −5 °C. Catalysts for dewaxing under hydrogenating conditions include H-ZSM-5 and Pt/H-mordenite [166], [180].

Another important process in oil refining is the isomerization of C_5/C_6 n-alkanes with Pt/H-mordenite or H-ZSM-5. Shell has combined this with the adsorptive separation of n- and iso-alkanes (UOP Isosiv process) to give the TIP process (total isomerization process) [173].

The zeolites Pt/K-L and Pt/BaK-L may be used in the future for dehydrocyclization, especially of C_6/C_7 alkanes, as conventional reforming catalysts (e.g., Pt/Cl – Al$_2$O$_3$) show poor selectivity in this range [173], [181]. Problems still arise from sensitivity of the new catalysts towards poisoning by sulfur. M-forming is operated as a post-reforming process with H-ZSM-5 as catalyst. This consists of shape-selective cracking of n-alkanes with simultaneous alkylation of benzene and toluene by the short-chain alkenes produced [166], [182].

Conversion of Gases. Both methanol from synthesis gas and LPG (liquefied petroleum gas) are raw materials for mineral oils and petrochemical products. Shape-selective reactions, catalyzed mainly by the zeolite ZSM-5, make these conversions possible.

The MTG (methanol to gasoline) process developed by Mobil [183], [184] and used in New Zealand to produce gasoline from methanol aroused much interest in the past. Investigations into the mechanism have shown that the methanol is first converted by the catalyst H-ZSM-5 into the intermediate dimethyl ether by splitting off water, and then into short-chain alkenes. These form oligomers which undergo conversion into alkanes/cycloalkanes and aromatics by hydrogen transfer and cyclization. However, more recently, processes to obtain gasoline di-

rectly from synthesis gas with the aid of zeolite catalysts are being developed.

In the MTO (methanol to olefins) process, which is closely related chemically to the MTG process, the object is to obtain C_2-C_4 alkenes from methanol. Possible catalysts for this process include ZSM-5, narrow-pore zeolites of the erionite or chabazite type, and structurally modified silicoaluminophosphates (SAPO-17, SAPO-34, and SAPO-44) [185]. The short-chain alkenes obtained can be converted into middle distillates in zeolite-catalyzed processes such as MOGD (Mobil olefin to gasoline and distillates) or SPGK (Shell poly gasoline and kero) [166], [173].

The CYCLAR process, recently developed jointly by UOP and BP, uses a Ga-ZSM-5 catalyst to synthesize aromatics from LPG (C_3/C_4 alkanes), which is available in abundance [186], [187].

Petrochemistry and Synthesis of Organic Intermediates. The prospect of producing petrochemicals and organic intermediates in shapeselective catalytic processes has led to intensive research [188–190]. This work was to some extent also motivated by the fact that some large-scale processes are increasingly under pressure for environmental reasons, e.g., processes using acid catalysts such as H_2SO_4, HF, H_3PO_4 on silica, and $AlCl_3$. Unlike these acids, zeolite catalysts are noncorrosive.

Typical zeolite-catalyzed reactions which have led to industrial processes include the alkylation of aromatics with alkenes, the disproportionation of alkyl- and chlorobenzenes, the isomerization, oligomerization, and hydration of alkenes, and the formation of amines from alcohols and ammonia. Relatively new reactions include oxidations using hydrogen peroxide as the oxidizing agent and the molecular sieve titanium silicalite-1 as the catalyst, e.g., the hydroxylation of aromatics, the ammoxidation of ketones, and the epoxidation of alkenes [24], [191].

A selection of processes which have been operated on an industrial scale are listed in Table 6 [166], [192]. Of these, the production of ethylbenzene by the reaction of ethene with benzene (Mobil – Badger process) and the isomerization of xylenes are the most important processes [166].

Environmental Protection. Advances have been made in the use of zeolitic catalysts for selective catalytic reduction of NO_x to nitrogen in the exhaust gases of lean-burn and diesel engines [201–204]. Metal-modified zeolites, especially Cu-ZSM-5 materials, have been intensively investigated. Suitable reducing agents include hydrocarbons, oxygen-containing, water-miscible organic compounds, and CO and H_2. However, the durability of the new catalyst under working conditions is still insufficient for broad application. Therefore, for the moment only stationary systems and mobile systems with diesel engines, where the heat and water-vapor stress is comparatively low, will be equipped with these catalysts [204]. Special zeolites have also been used for the reduction of NO_x with ammonia in commercial applications [205].

7.4. Other Uses

Zeolites can act as carriers or reservoirs for reactive substances. For example, zeolites containing silver, copper, or zinc are used commercially as antibacterial powders applied in manmade fibers for textiles for domestic or personal use [206], [207].

8. Economic Aspects of Synthetic Zeolites

Since synthetic zeolites have become available in commercial quantities, world consumption of these materials has greatly increased. Starting from a few hundred tonnes in the late 1950s, this became 60×10^3 t/a in 1975, 460×10^3 t/a in 1987 [91], and ca. 1.2×10^6 t/a in 1994. An overview of the important producers of zeolites for various application fields is given in Table 7.

Although the main use of zeolites was initially adsorption, detergent builders now represent the largest application quantitatively, 1 050 000 t/a or almost 90 % of zeolites produced in 1994 having been used for this purpose. Of this, ca. 950 000 t/a was zeolite NaA, and ca. 100 000 t/a NaP, a material which has only more recently been used in detergent formulations. In Japan and Western Europe, zeolites have increasingly replaced phosphates as

Table 6. Zeolite catalysts in petrochemical processes and processes for the production of organic intermediates

Process	Zeolites	Process developer	Refs.
Production of ethylbenzene from benzene and ethylene	H-ZSM-5	Mobil-Badger	[166]
Production of cumene from benzene and propene (liquid phase)	HY	Chemical Research & Licensing Co.	[193]
Production of p-ethyltoluene from toluene and ethylene	Modified ZSM-5	Mobil	[166]
Isomerization of xylene	Pt/H-ZSM-5 Pt/H-Mordenite	Mobil and others	[166]
Disproportionation of toluene to produce xylene	H-Mordenite ZSM-5	Mobil UOP/Toray	[166]
Production of m-chlorotoluene, m-di-chlorobenzene and 2,6-dichlorotoluene by isomerization processes	H-ZSM-5 H-Mordenite	Toray	[194]
Amination of methanol by ammonia to give dimethylamine as the principal product	Na/H-Mordenite	Nitto	[195], [196]
Hydration of cyclohexene to cyclohexanol	H-ZSM-5	Asahi	[196], [197]
Production of pyridine from acetaldehyde, formaldehyde, and ammonia	H-ZSM-5	Nepera	[198]
High-purity isobutene from MTBE	B-ZSM-5	Snamprogetti	[199]
Cyclohexanone oxime by ammoximation of cyclohexanone	Titanium silicalite-1	Enichem	[24], [191], [200]
Hydroxylation of phenol to hydroquinone/catechol	Titanium silicalite-1	Enichem	[24], [191]

detergent builders since the late 1970s. In the United States, this development was interrupted in 1983, but since 1987 detergents with zeolite-containing formulations have been increasingly used there also. In 1994, ca. 55 % of all detergent zeolites were consumed in Western Europe, 30 % in the United States, and 15 % in the Far East (mainly Japan, Taiwan, and Korea).

Compared with the enormous consumption of detergent zeolites, the use of zeolites for catalytic purposes seems small, the world total for 1994 being 115 000 t/a. However, when applying monetary criteria, it must be remembered that the value addition achieved by the use of catalysts greatly exceeds the cost of the catalysts themselves [192]. Of the zeolites used in catalysts, type Y zeolites occupy a dominant position (ca. 105 000 t/a), and of this, 100 000 t/a is a constituent of FCC catalysts alone. This figure is based on an average content of 25 % Y zeolite in the catalyst. Approximately 5000 t/a is used in catalysts for hydrocracking and other special processes. The consumption of ZSM-5 zeolites for the purposes mentioned in Section 7.3 is ca. 3000 t/a, and of synthetic mordenite 600 t/a. Other zeolites are quantitatively of minor significance.

The zeolites used in adsorption are mainly types A and X. The total zeolite consumption for the diverse individual uses (see Section 7.2)

was estimated to be ca. 50 000 t/a in 1994. Over half the catalysts and adsorbents that contain zeolites are produced and used in the United States. Western Europe and Eastern Asia follow some way behind.

Table 7. Synthetic-zeolite producers

Application	Zeolites	Producers
Detergent builders	NaA	Degussa AG (DE), Enimont (IT), Ethyl Corporation (US), Henkel KGaA (DE), Mizusawa Industrial Chemicals (JP), The PQ Corporation (US), Soprolit SA (BE), Zeochem SA (BE)
	NaP	Crosfield Chemicals (GB)
Catalysis	Y zeolites	Akzo Chemicals BV (NL), Catalysts & Chemical Ind. Corp. (JP), Engelhard Corporation (US), W.R. Grace & Co. (US), The PQ Corporation/Zeolyst Enterprises (US), UOP (US)
	ZSM-5, mordenite, and other specialty zeolites	ALSI-Penta Zeolithe GmbH (DE), CU Chemie Uetikon AG (CH), Degussa AG (DE), Eka Nobel AB (SE), Engelhard Corporation (US), Mobil Corporation (US), Südchemie (DE), Tosoh Corporation (JP), UOP (US)
Adsorption	A, X, specialty zeolites	Bayer AG (DE), Ceca SA (FR), Degussa AG (DE). W.R. Grace & Co. (US), CU Chemie Uetikon AG (CH), UOP (US), Tosoh Corporation (JP). Zeochem Company (US)

9. Toxicology

Epidemiological [208] and experimental investigations [209], [210] have shown that natural erionite, as found in Cappadocia (Turkey), can cause formation of mesotheliomas and bronchial carcinomas. The oncogenic activity of these minerals is explained in a similar way to that of asbestos, which has a fibrous crystal morphology. This crystal form is extremely rare in zeolites.

Natural erionite is so far the only example of a zeolite with toxic effects. A review can be found in [211]. Zeolite NaA, which is used as a detergent builder, was found to have negligible acute, subacute, chronic, or inhalative toxicity in comprehensive tests [66], [93], [212]. Furthermore, regular medical checkups of workers exposed to zeolite NaA for a period of years in production areas gave no indication whatever of fibrogenic or silicogenic effects [66]. In Germany, the MAK is 6 mg/m^3, i.e., the general dust threshold [93], [213].

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APPENDIX B

The active sites in different TS-1 zeolites for propylene epoxidation studied by ultraviolet resonance Raman and ultraviolet visible absorption spectroscopies

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The titanium species in four kinds of titanium-containing MFI zeolites have been studied by ultraviolet (UV)-Raman and ultraviolet visible (UV-Vis) absorption spectroscopies and by the epoxidation of propylene with diluted H_2O_2 solution (30%). UV-Raman spectroscopy is proved to be a suitable means to estimate qualitatively the framework titanium in TS-1 zeolites. Based on the comparison of the relative intensity ratio I_{1125}/I_{380} of UV-Raman spectra, the TS-1(conv.) sample synthesized hydrothermally by the conventional procedure shows the highest amount of framework titanium. UV-Vis spectroscopy reveals that besides minor anatase, titanium species are mainly tetrahydrally coordinated into the framework for TS-1(conv.) or the Ti-ZSM-5 sample prepared by gas–solid reaction between deboronated B-ZSM-5 and $TiCl_4$ vapor at elevated temperatures. For the TS-1(org.) and TS-1(inorg.) samples synthesized hydrothermally using tetrapropylammonium bromide (TPABr) as template and tetrabutylorthotitanite (TBOT) and $TiCl_3$ as titanium source, respectively, the presence of mononuclear and isolated TiO_x species which are proposed to bond to the zeolite extraframework is observed. In addition to the framework titanium species, these isolated TiO_x species are assumed to be also active for propylene epoxidation.

KEY WORDS: titanium silicalite; UV-Raman spectroscopy; UV-Vis absorption spectroscopy; mononuclear and isolated TiO_x; propylene epoxidation

1. Introduction

Because of its remarkable catalytic activity in selective oxidation of organic compounds under mild conditions, especially the use of diluted H_2O_2 as oxidant, titanium silicalite TS-1 has received much attention during the last decade [1–3]. Studies on the coordinated state of titanium ions and the reaction mechanism are the hot points since the synthesis of TS-1. Ti^{4+} ions in the framework isolated from each other by the silicalite matrix are commonly supported to be the active centers in the catalyzed oxidation, while crystalline anatase TiO_2 can only catalyze the H_2O_2 decomposition. For TS-1 the structure of active sites and the oxidation mechanism are mainly studied with tetrahedral Ti^{4+} ions in zeolite framework only [2,3]. However, in many but not all cases, another titanium species which is identified by a 250–290 nm band in the UV-Vis spectra of Ti-containing zeolites unexpectedly appears during the crystallization of Ti-containing zeolites [4–7]. The exact function, particularly in catalyzed oxidation, of this part of titanium species characterized by 250–290 nm UV-Vis absorption has not been investigated systematically.

Recently, UV-Raman spectroscopy was first used by us [8] to identify framework titanium in TS-1 zeolite. This technique can successfully avoid the fluorescence interfer-

ence from zeolite samples, so the Raman spectrum in the UV region gives better signal-to-noise ratio than in the visible region [9–11]. Most importantly, the Raman bands directly associated with the framework titanium species Ti–O–Si in zeolite can be selectively enhanced owing to the resonance Raman effect. UV-Vis spectroscopy, depending on its clear assignment of the absorption bands and relatively simple experimental technique, is a routine method for characterization of almost all types of Ti-containing zeolites. In this paper, using UV-Raman and UV-Vis spectroscopies, we characterize four kinds of Ti-containing MFI zeolites synthesized by different procedures and raw materials. The different titanium species in each Ti-containing MFI are distinguished and the catalytic properties of the Ti-containing samples for propylene epoxidation are discussed.

2. Experimental

2.1. Zeolite synthesis

The TS-1(conv.) sample was synthesized hydrothermally by a conventional procedure described in [1], while the other two TS-1 samples (TS-1(org.) and TS-1(inorg.)) were synthesized hydrothermally following the modified procedures created in our laboratory at Dalian University of Technology [12,13]. The employed raw materials for the synthesis of the three TS-1 samples and the samples designation are listed in table 1.

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Table 1
The employed raw materials for the synthesis of TS-1 and the sample notations.

Sample	Employed raw materials			Ref.
	Silicon source	Titanium source	Template	
TS-1(conv.)	Tetraethylortho silicate (TEOS)	Tetraethylortho titanate (TEOT)	Tetrapropylammonium hydroxide (TPAOH)	[1]
TS-1(org.)	Silica sol.	Tetrabutylortho titanate (TBOT)	Tetrapropylammonium bromide (TPABr)	[12]
TS-1(inorg.)	Silica sol.	TiCl$_3$	TPABr	[13]

The SiO$_2$/TiO$_2$ molar ratio 33 in gel was obtained for all three kinds of TS-1 samples.

The Ti-ZSM-5 sample was prepared by gas–solid reaction between deboronated B-ZSM-5 and TiCl$_4$ vapor at elevated temperature. The detailed preparation procedure was described elsewhere [14,15]. The B-ZSM-5 sample was first synthesized according to the literature [16], with SiO$_2$/B$_2$O$_3$ molar ratio 10 in mixed gel. After pretreatment with 2 M HCl solution at 80 °C, the deboronated B-ZSM-5 sample was adopted as precursor for the gas–solid reaction.

2.2. Characterization

UV-Raman spectra were recorded on a home-made UV-Raman spectrometer built at State Key Laboratory of Catalysis (Dalian Institute of Chemical Physics, PR China). The spectral resolution was estimated to be 1.0 cm^{-1} and the acquisition time is 10 min. UV-Vis spectra were recorded on a Shimadzu UV240 spectrometer, and a pure powdered MgO sample was used as a reference. FT-IR spectra were obtained on a Nicolet 20 DXB spectrometer, and KBr pellet technique was adopted. XRD was performed on a Shimadzu XD-3A diffractometer (Cu K$_\alpha$).

2.3. Catalytic activity

The propylene epoxidation was carried out in a 200 ml stainless-steel autoclave equipped with a magnetic stirrer, a constant temperature water bath, an inlet for gas reagent and an outlet for exhausting gas. For a typical run, 0.4 g catalyst, 31.6 ml methanol and 3.0 ml H$_2$O$_2$ (30%) were charged into the autoclave. The reaction was started when the slurry was heated at 333 K under pressure of propylene (0.4 MPa) by vigorously stirring. Products were analyzed by a gas chromatograph (ShangFen 1102), using a flame ionization detector and a capillary column (30 m × 0.25 mm) containing polyethylene glycol as the stationary phase. The amount of unreacted H$_2$O$_2$ was determined by iodometric titration. The efficiency of H$_2$O$_2$ was calculated as the amount of H$_2$O$_2$ consumed in the formation of the oxidized products. The selectivity to propylene oxide (PO) referred to the content of PO in the oxidized products.

3. Results and discussion

3.1. Synthesis of different Ti-containing MFI zeolites

Four kinds of titanium-containing MFI zeolites were prepared by different procedures. The XRD patterns show
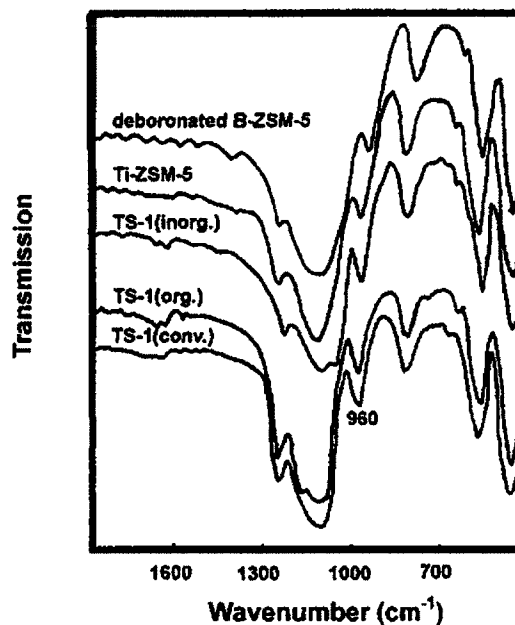

Figure 1. FT-IR spectra of Ti-containing MFI zeolites and deboronated B-ZSM-5 precursor.

that samples synthesized by the hydrothermal method possess perfect MFI structure and high crystallinity. For the Ti-ZSM-5 sample, the XRD pattern matches well with that of the deboronated B-ZSM-5 precursor, despite a decrease of about 10% crystallinity after gas–solid reaction. FT-IR spectra (figure 1) show the band at 960 cm^{-1} for each Ti-containing zeolite. This band has been widely used to characterize the incorporation of titanium in the framework lattice. Although the exact assignment of the 960 cm^{-1} band is controversial, it seems likely that this band corresponds to the stretching Si–O vibration mode perturbed by the neighboring Ti^{4+} ions [3].

For the deboronated B-ZSM-5 sample, a band at 920 cm^{-1} appears. This band is assigned to Si–OH groups in the silanol nests, which are created by the emigration of boron from the zeolite framework [14,17]. After the gas–solid reaction between the deboronated B-ZSM-5 precursor and TiCl$_4$ vapor, the 920 cm^{-1} band is shifted to 960 cm^{-1}. The IR results directly indicate the insertion of titanium in the zeolite framework [14].

Different from the TS-1(conv.) sample prepared by the conventional method in which TPAOH is used as the template, the TS-1(org.) and TS-1(inorg.) samples are synthe-
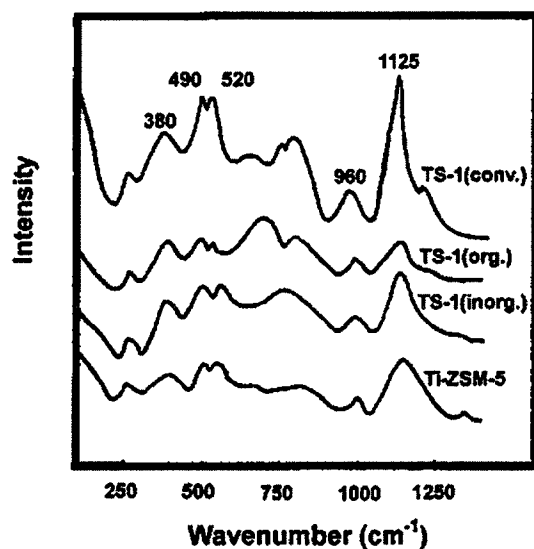
Figure 2. UV-Raman spectra of Ti-containing MFI zeolites.

Table 2
Comparative characterization of Ti-containing MFI zeolites by UV-Raman and UV-Vis spectroscopies.

Sample	I_{1125}/I_{380} ratio of UV-Raman spectra	Predominant bands in UV-Vis		
		210 or 225 nm	280 nm	330 nm
TS-1(conv.)	5.2	Strong	–	Strong
TS-1(org.)	1.2	Strong	Strong	Very weak
TS-1(inorg.)	3.2	Strong	Weak	Very weak
Ti-ZSM-5	3.5	Strong	–	Weak

sized by modified procedures using TPABr as template. Recently, instead of the use of the relative expensive template TPAOH, TPABr with one kind of organic or inorganic ammonium (e.g., 1,6-hexamethylene diamine, n-butylamine, $NH_3 \cdot H_2O$) has been adopted as a cheaper template system in the TS-1 synthesis in order to decrease the synthesis cost [12,13,18,19]. The studies show that, when the $TPABr/SiO_2$ ratio in the mixed gel is above 0.05, the additional organic or inorganic ammonium can only act as a base to regulate the pH value in the gel.

3.2. UV-Raman spectroscopy

Figure 2 shows the UV-Raman spectra of the four kinds of Ti-containing MFI samples. Three resonance enhanced Raman bands at 490, 520 and 1125 cm^{-1} are observed exclusively for these samples, and the relative intensities of these bands, especially the one at 1125 cm^{-1}, are quite different from each other. The 490, 520 and 1125 cm^{-1} bands are the characteristics of the framework titanium species in the TS-1 sample and these bands increase in intensity with the crystallization time of TS-1 [8]. A band at 380 cm^{-1} also appears for each sample. This band is supposed to be the identification of the MFI stucture [8]. Table 2 shows that, TS-1(conv.) synthesized by the conventional method using TPAOH as template can obtain the highest intensity
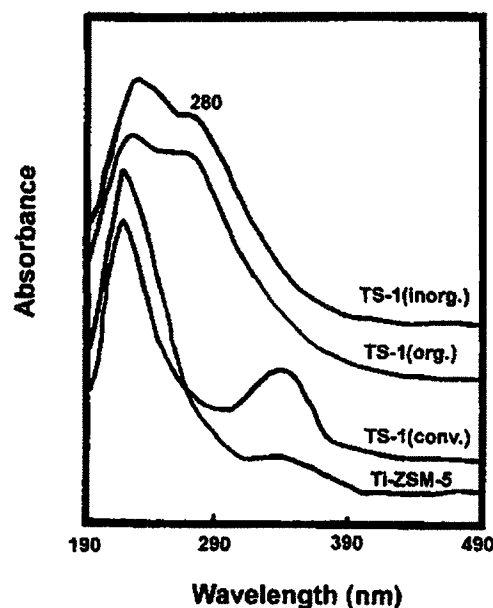

Figure 3. UV-Vis spectra of Ti-containing MFI zeolites.

ratio I_{1125}/I_{380} of 5.2, which indicates that TS-1(conv.) possesses the largest amounts of titanium in its framework in comparison with TS-1(org.) and TS-1(inorg.). The results of UV-Raman spectra suggest that very effective insertion of titanium into the framework can be obtained by using TPAOH as template during the synthesis of TS-1.

Compared to TS-1(org.) synthesized using TBOT as titanium source, the TS-1(inorg.) sample using $TiCl_3$ as titanium source possesses a higher I_{1125}/I_{380} ratio of 3.2 than that of 1.2. It can be proposed that inorganic titanium source $TiCl_3$ can match well with the inorganic silicon source silica sol. during the crystallization of TS-1. The relative intensity of the 1125 cm^{-1} band is almost identical for Ti-ZSM-5 and TS-1(inorg.), and both are lower than that for the TS-1 (conv.) sample.

3.3. UV-Vis spectroscopy

UV-Vis spectra of the Ti-containing MFI are shown in figure 3. Two main charge-transfer absorption bands around 210 and 330 nm are observed for the TS-1(conv.) and Ti-ZSM-5 samples. The former with absorption onset at about 270 nm is attributed to tetrahedrally coordinated framework titanium; the latter with absorption onset at about 390 nm is typical for anatase TiO_2. It can be seen that the relative intensity of the 330 nm band is much lower in Ti-ZSM-5 than in TS-1(conv.). The UV-Vis spectra of TS-1(org.) and TS-1(inorg.) show the similar absorption: Besides a band centered around 225 nm which is assigned to framework titanium, the absorption with a maximum at about 280 nm and an onset at 390 nm is observed. It can be seen that the band assigned to framework titanium species is shifted from 210 nm in TS-1(conv.) to 225 nm in TS-1(org.) and TS-1(inorg.). Compared to that of TS-1(conv.), the isolated

framework titanium in TS-1(org.) and TS-1(inorg.) may be loosely coordinated to the surrounding Si–O band, resulting in a shift of the framework titanium absorption maximum to higher wavelength. This implies that the local coordinated environment of part of the framework titanium in TS-1(org.) and TS-1(inorg.) is slightly different from that in TS-1(conv.) [4].

A broad band, with a maximum around 280 nm and an absorption onset at 390 nm is present in the UV-Vis spectra of TS-1(org.) and TS-1(inorg.). Although the exact assignment of the band around 280 nm is still under discussion, it can be accepted that these titanium species are quite different from tetrahedrally coordinated framework titanium characterized by the band about 210 nm. Three main types of structure of these non-framework titanium species, in the spectrum of TS-1 [4], Ti-β [5,6], Ti-ZSM-12 [7] or zeolite-hosted mononuclear titanium oxide species [20], have been proposed: (1) the formation of hexacoordinated species with two water molecules in the coordination sphere [4]; (2) the formation of partly aggregated hexacoordinated species, Ti–O–Ti [5–7]; and (3) the formation of isolated single-bonded TiO_x species attached to the zeolite lattice [20]. It can be seen that the relative intensity of the band around 280 nm in TS-1(org.) is stronger than that in TS-1(inorg.), which indicates that the former occupies more isolated or partly polymerized non-framework titanium species.

In comparison with TS-1(conv.), no obvious charge-transfer absorption at 330 nm in TS-1(org.) and TS-1(inorg.) is observed. However, the absorption onset of anatase at about 390 nm is also present. It seems that the signal of anatase in TS-1(org.) and TS-1(inorg.) spectra should be covered by the broad band around 280 nm.

For the sake of brevity, the observed UV-Vis bands of four kinds of Ti-containing zeolites are compared in table 2. Based on the above mentioned UV-Raman and UV-Vis results, it can be concluded that for TS-1(org.) and TS-1(inorg.), the coexistence of framework titanium, isolated or partly polymerized non-framework titanium, and anatase is observed, while only two kinds of titanium species, tetrahedral Ti^{4+} ions and anatase, are present in TS-1(conv.) and Ti-ZSM-5.

3.4. Epoxidation of propylene with diluted H_2O_2

A summary of the performance of the Ti-containing MFI in the epoxidation of propylene with diluted H_2O_2 is given in table 3. Both TS-1(conv.) and TS-1(org.) samples show higher H_2O_2 conversion and efficiency. The Ti-ZSM-5 sample gives the lowest H_2O_2 conversion and efficiency under the same reaction conditions. With framework Ti^{4+} only, many studies on TS-1 have discovered that the active centers in catalysis must be the Ti^{4+} in framework position isolated from each other by the silicalite matrix. The more Ti^{4+} species exist in the framework, the higher activity can be obtained for TS-1. In accordance with the above speculation, TS-1(conv.) having larger amounts of framework titanium (see figure 2 and table 2) can obtain higher H_2O_2 conversion and efficiency.
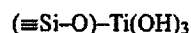
Table 3
The results of propylene epoxidation over Ti-containing MFI zeolites.[a]

Sample	Conv. of H_2O_2 (%)	Eff. of H_2O_2 (%)	Sel. for PO[b] (%)
TS-1(conv.)	94.0	86.6	97.9
TS-1(org.)	97.4	94.6	92.1
TS-1(inorg.)	84.1	90.2	94.5
Ti-ZSM-5	58.0	83.2	99.3

[a] Reaction conditions: catalyst 0.4 g, methanol 31.6 ml, H_2O_2 (30%) 3 ml, propylene pressure 0.4 MPa, 333 K, 1.5 h.

[b] PO: propylene oxide. The by-products are glycol and monomethyl ethers.

Surprisingly, the TS-1(org.) sample with the lowest intensity ratio I_{1125}/I_{380} in the UV-Raman spectrum can obtain 97.4% of H_2O_2 conversion and 94.6% of H_2O_2 efficiency. For the propylene epoxidation, a TiO_2/SiO_2 heterogeneous catalyst has been developed by Shell. The formation of the titanyl group $>Ti=O$ which is attached to vicinal silanol groups is suggested to explain the catalysis of this kind of catalyst in epoxidation [21]. According to Klaas et al. [20], the 290 nm band in the UV-Vis spectrum of zeolite-hosted mononuclear titanium oxide species is assigned to single-bonded TiO_x species, which are in a mononuclear and isolated way attached to the zeolite lattice. The structure of these TiO_x species can be described as follows:

$$(\equiv Si\text{–}O)\text{–}Ti(OH)_3$$

It is assumed that for TS-1(org.) the 280 nm band in the UV-Vis spectrum may correspond to such mononuclear and isolated TiO_x species. These TiO_x species are suggested to be transformed into the active titanyl group $>Ti=O$ structure after calcination. When reacted with H_2O_2, the titanyl group would produce surface titaniumhydroperoxo compounds, which would then react with propylene to produce the epoxide. It is proposed that the coexistence of two kinds of active sites: framework Ti^{4+} and highly isolated TiO_x species in TS-1(org.) cause the higher activity for propylene epoxidation.

Compared to TS-1(org.), TS-1(inorg.) with smaller content of TiO_x species obtains lower H_2O_2 conversion. Based on UV-Raman and UV-Vis spectroscopy, Ti-ZSM-5 occupies a low amount of framework Ti^{4+} and almost no isolated TiO_x species can be obtained. So, the conversion of H_2O_2 is lower for Ti-ZSM-5 in comparison with the other three TS-1 samples.

4. Conclusion

Four kinds of Ti-containing MFI zeolites have been synthesized by different procedures and raw materials. Using UV-Raman spectroscopy, framework titanium in these Ti-containing MFI is estimated qualitatively. The TS-1 (conv.) sample synthesized hydrothermally by the conventional method obtains the highest amount of framework titanium. The relative content of framework titanium in Ti-ZSM-5 prepared by gas–solid reaction is lower compared

to TS-1(conv.). UV-Vis spectra show that mononuclear and isolated TiO$_x$ species which are absent in the above two Ti-containing MFI, are observed in the TS-1(org.) and TS-1 (inorg.) samples synthesized hydrothermally by the modified procedure. Framework titanium, in combination with isolated TiO$_x$ species if existing in TS-1 are supposed to be the active sites for propylene epoxidation according to the characterization and reaction results.

Acknowledgement

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APPENDIX C

Synthesis and characterization of titanium-containing molecular sieves

Citation

Abstract

The use of zeolites and molecular sieves as catalysts for important organic reactions is reviewed. One emerging area of particular interest is the use of titanium-containing molecular sieves as partial oxidation catalysts and is chosen for further study.

In order to elucidate the relationships between the physicochemical properties of titanium-containing molecular sieves and their ability to act as partial oxidation catalysts, titanium-containing pure-silica ZSM-5 (TS-1) materials are synthesized using different methods. The activities of the titanium-containing catalysts for the oxidation of alkanes, alkenes, and phenol at temperatures below 100 [degrees]C using aqueous hydrogen peroxide H2O2 as the oxidant are reported. The relationships between the physicochemical and catalytic properties of these titanium silicates are discussed. The effects of added aluminum and sodium on the catalytic activity of TS-1 are described. The addition of sodium during the synthesis of TS-1 is detrimental to the catalytic activity while sodium incorporation into pre-formed TS-1 is not. The framework substitution of aluminum for silicon appears to decrease the amount of framework titanium.

The relationships between catalytic performance and physicochemical properties that are controlled through synthetic methods are further investigated using a series of titanium-containing molecular sieves. Titanium-containing pure-silica ZSM-5 (TS- 1), pure-silica ZSM-48 (Ti-ZSM-48) and zeolite beta (Ti-Al-beta) are synthesized and characterized by X-ray powder diffraction (XRD), elemental analysis, physical adsorption of N2, Fourier transform infrared (FT-IR), FT-Raman, and diffuse reflectance ultraviolet (DR-UV) spectroscopies. TS-1 is synthesized by five different methods. All materials are evaluated for their ability to oxidize 1-hexene and n-octane using aqueous H2O2 as the oxidant. The relationships between the physicochemical and catalytic properties of these titanium-containing zeolites are discussed. TS-1 samples synthesized at high pH are catalytically active and framework titanium is shown to be necessary for olefin epoxidation and alkane hydroxylation to occur. The existence of anatase in active TS-1 samples results in decreased hydrogen peroxide efficiencies in the epoxidation reaction. TS-1 produced at pH=7.4 and Ti-ZSM-48 each contain anatase and are not active. Ti-beta is found to contain framework titanium and be free of anatase. However, at the conditions used in this study these samples are not able to activate 1-hexene or n-octane.

In attempts to prepare large pore titanium-containing molecular sieves, postsynthetic incorporation of titanium in the borosilicate SSZ-33 and the direct synthesis of an aluminum-free

titanium-containing zeolite Beta (Ti-Beta) are reported. These materials are characterized by XRD, FT-IR, FT-Raman, and DR-UV spectroscopies. The molecular sieves are shown to catalyze the epoxidation of various olefins using aqueous hydrogen peroxide as the oxidant. The physicochemical properties as found by the characterization methods are correlated to the catalytic data and the results compared to a high quality sample of TS-1. The modified SSZ-33 samples contain titanium primarily in the form of isolated tetrahedrally coordinated Ti atoms, although some extra-framework Ti is observed by Raman and DR-UV spectroscopies. Ti-Beta samples show no evidence of extra-framework titanium. For the epoxidation of cis-cyclooctene, the Ti-Beta catalysts give quantitative conversion to epoxide, and both the Ti-Beta and Ti-SSZ-33 catalysts are able to epoxidize substrates too large to be oxidized by TS-1.

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